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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C08F 10/00, 4/54, B01J 31/18, 31/16		A1	(11) International Publication Number: WO 98/40421
			(43) International Publication Date: 17 September 1998 (17.09.98)
(21) International Application Number: PCT/US98/04895			(81) Designated States: CA, DE, GB, JP, KR, MX, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(22) International Filing Date: 12 March 1998 (12.03.98)			
(30) Priority Data: 08/818,297 14 March 1997 (14.03.97) US 60/068,641 23 December 1997 (23.12.97) US 09/033,489 3 March 1998 (03.03.98) US			
(71) Applicant: UNIVERSITY OF IOWA RESEARCH FOUNDATION [US/US]; Oakdale Research Campus, 100 Oakdale Campus #214, Iowa City, IA 52242-5000 (US).			
(72) Inventors: JORDAN, Richard, F.; Oakdale Research Campus, 100 Oakdale Campus #214, Iowa City, IA 52242-5000 (US). COLES, Martyn, P.; Oakdale Research Campus, 100 Oakdale Campus #214, Iowa City, IA 52242-5000 (US).			
(74) Agent: SEASE, Edmund, J.; Zarley, McKee, Thornte, Voorhees & Sease, Suite 3200, 801 Grand Avenue, Des Moines, IA 50309-2721 (US).			
(54) Title: CATIONIC GROUP 13 COMPLEXES INCORPORATING BIDENTATE LIGANDS AS POLYMERIZATION CATALYSTS			
(57) Abstract Disclosed are novel catalysts, processes of synthesizing the catalysts and olefin polymerization processes using the catalysts. The catalysts are cationic complexes comprising a Group 13 element and certain ligands. These compounds behave similarly to Ziegler-Natta catalysts but effectively catalyze the polymerization of olefins in the absence of any transition metal.			

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**CATIONIC GROUP 13 COMPLEXES INCORPORATING
BIDENTATE LIGANDS AS POLYMERIZATION CATALYSTS**

BACKGROUND OF THE INVENTION

5 Ziegler-Natta type catalysts for polymerization of unsaturated hydrocarbons, such as alpha olefins, have long been the state of the art catalysts for such reactions. Typically, Ziegler-Natta type catalysts are composed of transition metal salts and aluminum alkyl compounds, e.g.,
10 titanium tetrachloride and triethylaluminum. While these catalysts are very effective and have a long-established record of use, they are not without drawbacks. For example, transition metals are expensive, potentially present some toxicity hazards, and to some are environmentally
15 objectionable. Therefore, efforts towards the development of alternative, suitable olefin polymerization catalysts have occurred. For example, metallocene catalysts have been developed for use in alpha olefin polymerization. The polymerization of ethylene using an aluminum-based catalyst
20 but in the absence of a transition metal is known. For example, the formation of polyethylene by the polymerization of ethylene in the presence of catalysts prepared by the reaction of neutral aluminum compounds, such as $\text{Cl}_2\text{AlCH}(\text{Me})\text{AlCl}_2$ or $(\text{AlR}_3)_2$, with ethylene at a temperature in
25 the range of 25 to 50°C has been reported by H. Martin and H. Bretinger, *Makromol. Chem.* **1992**, 193, 1283. However, the reported catalytic activities are very low ($1.6 \times 10^{-1} - 3.8 \times 10^{-4}$ g PE/(mol·h·atm)).

30 The present invention has as its primary objective the development of more highly active catalysts useful for the polymerization of unsaturated hydrocarbons which do not require a transition metal compound as a component of the catalyst.

35 Another objective of the present invention is to prepare such catalysts in high yields using convenient and practical synthetic methods.

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A yet further objective of the present invention is a method for polymerizing unsaturated hydrocarbons using the novel, transition metal-free catalysts provided by this invention.

The method and manner of accomplishing each of the above objectives, as well as others, will become apparent from the detailed description of the invention which follows hereinafter.

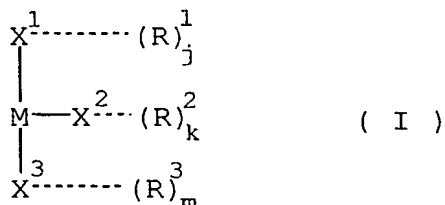
SUMMARY OF THE INVENTION

This invention relates to novel catalysts, processes of synthesizing the catalysts and to olefin polymerization processes using the catalysts. The catalysts are cationic complexes comprising a Group 13 element and certain ligands.

These compounds behave similarly to Ziegler-Natta catalysts but effectively catalyze the polymerization of olefins in the absence of any transition metal.

DETAILED DESCRIPTION OF THE INVENTION

We have discovered that the compositions defined below are effective catalysts for the polymerization of olefins. Therefore, one embodiment of the present invention is represented by a catalyst composition comprising components (1), (2) and (3) wherein component (1) is a Lewis acid having the formula:



wherein

M is an atom selected from the Group 13 elements, i.e., a boron, aluminum, gallium, indium or thallium atom;

X¹, X² and X³ are the same or different and each is selected from hydrogen and the elements of Groups 14, 15, 16

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and 17;

R^1 , R^2 and R^3 are the same or different and each is selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, nitrogen or oxygen-containing heterocyclic, silyl, siloxy groups or metallic groups such as Al(III), Mg(II) and two groups (R^1 , R^2 or R^3) may be combined to form with X^1 , X^2 , or X^3 a cyclic group; and

j , k and m are the same or different and may be 0, 1, 2 or 3 as required to satisfy the valence of each of atoms X^1 , X^2 and X^3 to which R^1 , R^2 and R^3 , respectively, are bound;

component (2) is a Lewis-base having the formula $Y(R^4)_n$ wherein Y is an atom selected from the Group 15 and 16 elements; R^4 represents up to 3 substituents which may be the same or different and are selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, silyl, alkoxy, aryloxy and amino; n is 1, 2 or 3 as required to satisfy the valence of Y to which R^4 is bound; and two groups, R^4 , may be attached so as to form a cyclic structure as found in tetrahydrofuran ($Y = O$, $(R^4)_2 = (CH_2)_4$) or pyridine ($Y = N$, $(R^4)_2 = (CH)_5$); and

component (3) is an activator selected from (a) a salt of a labile, non-coordinating or weakly coordinating anion that is capable of replacing one of the $-X^1--(R^1)_j$, $-X^2--(R^2)_k$ or $-X^3--(R^3)_m$ groups of component (1); (b) a neutral Lewis acid that is capable of abstracting one of the $-X^1--(R^1)_j$, $-X^2--(R^2)_k$ or $-X^3--(R^3)_m$ groups from component (1); (c) an oxidizing agent capable of reacting with component (1) and converting it to a cationic derivative; and (d) alumoxanes.

The hydrocarbyl group which R^1 , R^2 , R^3 and/or R^4 may represent may be a saturated or unsaturated, unsubstituted or substituted, aliphatic, alicyclic, heterocyclic or aromatic group containing up to about 50 carbon atoms, preferably up to about 12 carbon atoms. Examples of the substituents which may be present on the substituted hydrocarbyl groups include methyl, ethyl, isopropyl, isobutyl, t-butyl, neopentyl, alkoxy, and halogen. Examples

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of the aromatic groups which R^1 , R^2 , R^3 and/or R^4 may represent include, phenyl, naphthyl, and anthracenyl with substituents selected from methyl, ethyl, isopropyl, t-butyl, silyl, aryl, alkoxy, amino, or a halogen. The alkoxy or amino groups which R^1 , R^2 , R^3 and/or R^4 may represent may contain up to about 50 carbon atoms, preferably up to about 12 carbon atoms.

Examples of the groups represented collectively by $-X^1--(R^1)_j$, $-X^2--(R^2)_k$ and $-X^3--(R^3)_m$ include methoxy, ethoxy, isopropoxy, t-butoxy, phenoxy, thiophenoxy, N-methylanilino, diisopropylamino, bis(trimethylsilyl)amino, dimethylphosphido, dicyclohexylphosphido, diphenylphosphido, pivalate, N,N'-diisopropylacetamidinate, N,N'-dicyclohexylacetamidinate, N,N'-diadamantylacetamidinate, N,N'-bis(2,6-dimethylphenyl)acetamidinate, N,N'-diisopropylpivamidinate, N,N'-dicyclohexylpivamidinate, N,N'-diadamantylpivamidinate, N,N'-bis(2,6-dimethylphenyl)pivamidinate, t-butyl-N-isopropylcarbamate, t-butyl-N-isopropylthiocarbamate, diisopropyl-dithiocarbamate, N,N-dimethyl-N',N''-diisopropylguanadinate, N,N-diethyl-N',N''-diisopropylguanadinate, N,N-diisopropyl-N',N''-diisopropylguanadinate, N,N-bis(trimethylsilyl)-N',N''-diisopropylguanadinate, 1,3,4,6,7,8-hexahydro-2H-pyrimido-[1,2-a]pyrimidine, thiopivalate, dithiopivalate, N,N'-diadamantylthioureate, N,N'-bis(2,6-dimethylphenyl)thioureate, N,N'-bis(2,6-diisopropylphenyl)thioureate, and N,N'-bis(t-butyl)thioureate. The groups represented collectively by $-X^1--(R^1)_j$, $-X^2--(R^2)_k$ and $-X^3--(R^3)_m$ preferably are selected from N,N'-diisopropylacetamidinate, N,N'-dicyclohexylacetamidinate, N,N'-diadamantylacetamidinate, N,N'-diisopropylpivamidinate, N,N'-dicyclohexylpivamidinate, N,N'-diadamantylpivamidinate, N,N-dimethyl-N',N''-diisopropylguanadinate, N,N-diethyl-N',N''-diisopropylguanadinate, N,N'-diadamantylthioureate.

The most preferred groups represented by $-X^1--(R^1)_j$, $-X^2--(R^2)_k$ and $-X^3--(R^3)_m$ are N,N'-diisopropylpivamidinate, N,N'-dicyclohexylpivamidinate, N,N'-bis(adamantyl)piv-

amidinate.

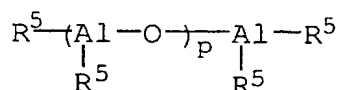
Examples of the Lewis-base compounds represented by $Y(R^4)_n$ include dimethyl ether, tetrahydrofuran, methyl-t-butylether, dimethylsulfide, trimethylamine, triethyl-amine, tributylamine, 2,6-lutidine, 2,4,6-collidine, N,N-dimethylaniline, 2,6-diisopropylaniline, trimethylphosphine, triethylphosphine, tricyclohexylphosphine, triphenylphosphine, and triphenylphosphite. The Lewis base is utilized in the range of 0 to 1000 molar equivalents relative to Component (1) with a minimum being preferred to minimize the competitive inhibition of polymerization. The Lewis base compound represented by $Y(R^4)_n$ preferably is selected from methyl-t-butylether, 2,6-lutidine, 2,4,6-collidine, N,N-dimethylaniline and 2,6-diisopropylaniline.

Examples of the component (3) activators include (1) salts of labile, non-coordinating or weakly coordinating anions that are capable of abstracting one of the $-X^1--(R^1)_j$, $-X^2--(R^2)_k$ or $-X^3--(R^3)_m$ groups from component (1) such as the alkali metal, silver, thallium, triphenylcarbenium, or anilinium salts of tetraphenylborate, tetrakis(pentafluorophenyl)borate; tetrakis[3,5-bis(trifluoromethyl)phenyl]borate, tetrafluoroborate, hexafluorophosphate, hexafluoroantimonate, perchlorate, trifluoromethanesulfonate, nonafluorobutylsulfonate, $(B_{12}H_{12})^{2-}$, $(CB_{11}H_{12})^-$, $(C_2B_9H_{12})^-$, or $[(C_2B_9H_{11})_2Co]^-$; (2) neutral Lewis acids that are capable of abstracting one of the $-X^1--(R^1)_j$, $-X^2--(R^2)_k$ or $-X^3--(R^3)_m$ groups from component (1) such as triphenylboron, tris(pentafluorophenyl)boron; tris[3,5-bis(trifluoromethyl)phenyl]boron, trialkylaluminum, and alumoxanes; (3) oxidizing agents capable of reacting with component (1) and converting it to a cationic derivative such as ferrocenium or silver salts of non-coordinating or weakly coordinating anions. These are typically applied in a molar ratio of Components (1):(3) from 1:0.001-100,000.

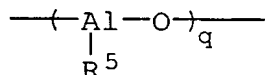
The activator alumoxanes are well known in the art and comprise oligomeric linear and/or cyclic alkyl alumoxanes

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represented by the formula:



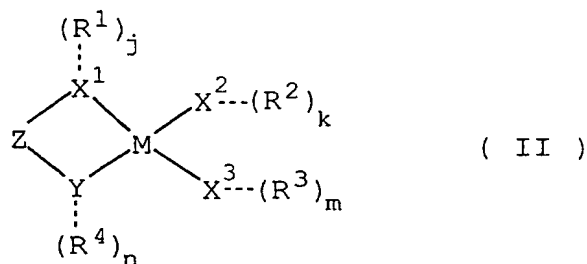
for oligomeric, linear alumoxanes and:



for oligomeric, cyclic alumoxane, wherein p is 1-40, preferably 10 - 20, q is 3 - 40, preferably 3 - 20, and R⁵ is an alkyl group of up to about 8 carbon atoms, preferably methyl. Generally, in the preparation of alumoxanes from, for example, trimethylaluminum and water, a mixture of linear and cyclic compounds is obtained.

The component (3) activator preferably is selected from tris(perfluorophenyl)boron, triphenylcarbenium [tetrakis(perfluorophenyl)borate], and alumoxanes and is preferably applied in a molar ratio of component (1):(3) of 1:0.1-1,000. Use of an excess of (3) is advantageous as a scavenger of surreptitious impurities.

Another embodiment of the present invention is a two-component catalyst composition comprising components (3), as described above, and (4), defined as a complex of a Group 13 metal having the formula:

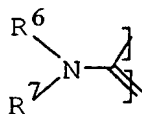


wherein M, X¹, X², X³, Y, R¹, R², R³, R⁴, j, k, m and n are defined above and Z is a saturated or unsaturated linking group, e.g., a methylene or methyldene group or a chain of 2 to 30 carbon atoms or 2 to 12 atoms comprising carbon and

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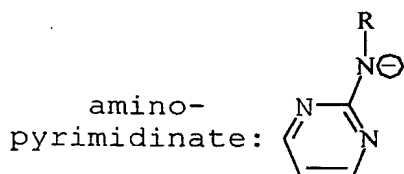
a second element selected from oxygen, sulfur or nitrogen. Examples of the linking groups represented by Z include ethylene, propylene, butylene, trimethylene, a group having the formula $=CHCH=CH-$, or aminomethylidene, which has the

5 formula:

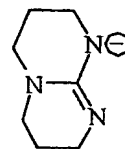


wherein R^6 and R^7 are the same or different and each is selected from hydrogen, hydrocarbyl, substituted hydrocarbyl or silyl groups. Groups R^6 and R^7 may form a cyclic moiety

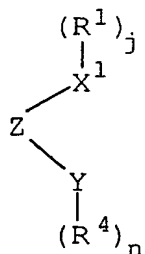
10 if a covalent network creates a second link between the bridge, Z, and atoms X^1 or Y. Pyrimidates illustrate such structures:



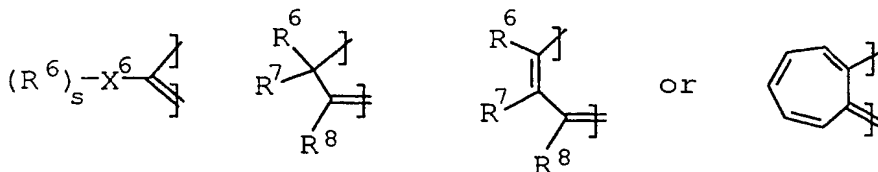
hexahydro-pyrimido-pyrimidinate:



Examples of the residues represented by



15 include residues in which Z is a bridging group having the structure:



wherein R^6 , R^7 and R^8 are the same or different and each is

selected from hydrogen, a hydrocarbonyl group and a silyl group; X^6 is an oxygen, nitrogen, carbon or silicon atom; and s is 1, 2, or 3 as required to by the valence of X^6 . Figure 1 depicts examples of residues which may be represented by
 5 $(R^1)_j X^1-Z-Y(R^4)_n$.

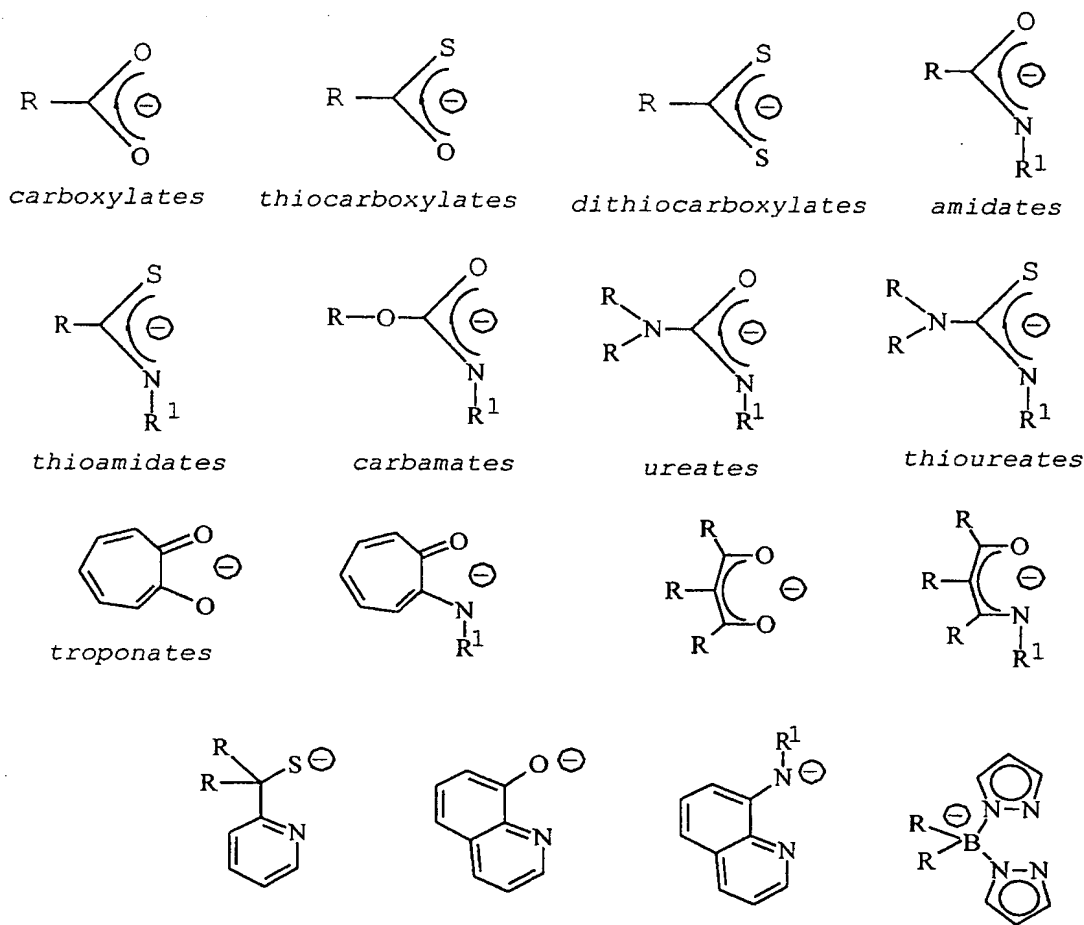


Figure 1. Examples of $(R^1)_j X^1-Z-Y(R^4)_n$ as in Formula (II). R indicates a generic substituent while R^1 is bound to X^1 .

10 Residues in which both X^1 and Y are nitrogen atoms, j and $n = 1$, and R^1 and R^4 are alkyl, aryl, or silyl groups are preferred (see Figure 2).

15 In addition, groups R^1 and R^4 that impart a steric encumbrance to the coordination sphere of the metal ligated to X^1 and Y are further preferred. Examples of the latter include alkyl groups bound to X^1 or Y by secondary or

tertiary carbons such as isopropyl, cyclohexyl, t-butyl, and adamantyl; aryl groups with substitution in the ortho position such as 2,6-dimethyl-phenyl and 2,6-diisopropylphenyl; and trisubstituted silyl groups such as trimethylsilyl. Other examples will be apparent to those skilled in the art.

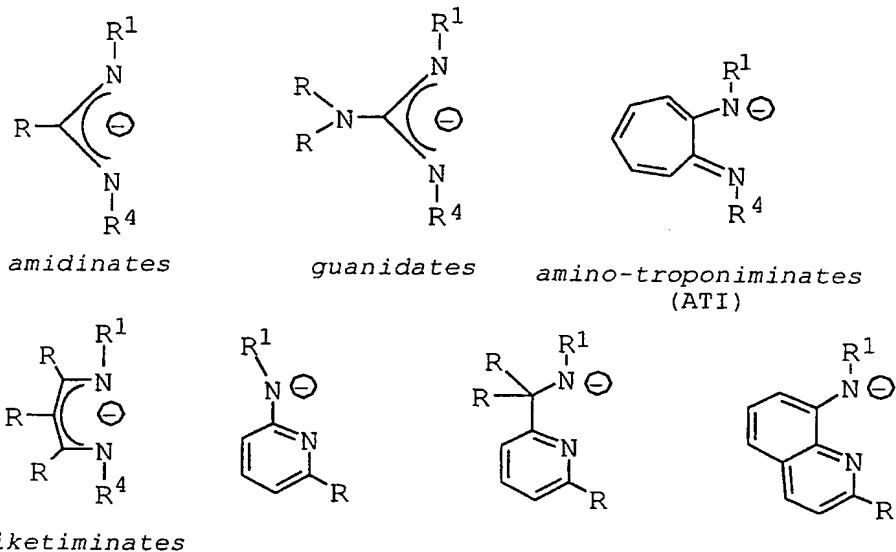
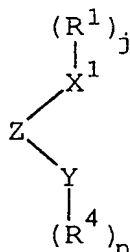


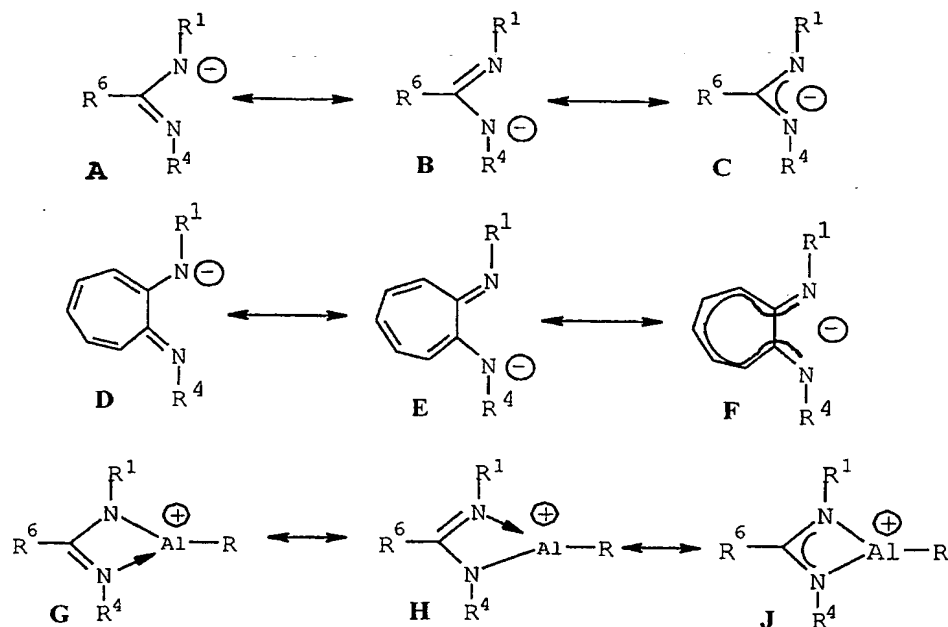
Figure 2. Examples of preferred residues, $(R^1)_jX^1-Z-Y(R^4)_n$. R^1 is bound to X^1 , R^4 to Y , and R is a generic substituent.

In cases where the bridging group Z is unsaturated the anionic residues represented by



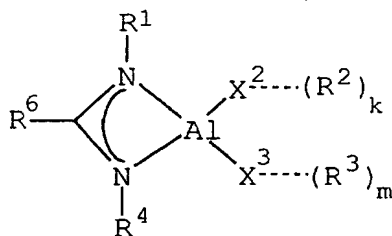
15 may be depicted by the resonance hybrid of their localized resonance structures. For example, the amidinate ligands may be represented by structure C, which is the resonance hybrid of localized resonance structures A and B. Similarly, the aminotroponimate ligand may be depicted as

structure F, which is the resonance hybrid of D and E and the base-free cationic aluminum amidinate complexes may be represented by structure J, which is the resonance hybrid of localized resonance structures G and H.



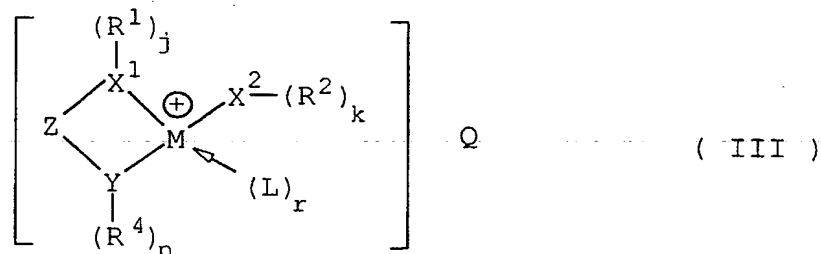
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A preferred embodiment of the complexes of formula (II) are aluminum amidinate compounds having the formula:

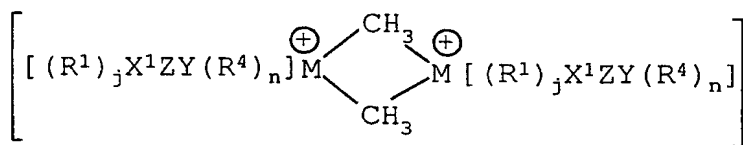


wherein R¹, R⁴, and R⁶ are selected from the groups consisting of C₁ to C₅₀ alkyl, aryl or silyl, such as methyl, ethyl, i-propyl, t-butyl, cyclohexyl, adamantyl, phenyl, 2,6-dimethylphenyl, 2,6-diisopropylphenyl, 2-t-butylphenyl and -X²--(R²)_k and -X³--(R³)_m are selected from the groups consisting of hydrogen, methyl, ethyl, isobutyl, neopentyl, benzyl, phenyl, or halogen.

A third embodiment of the present invention comprises a single-component catalyst having the formula:



wherein M, X¹, X², R¹, R², R⁴, j, k, n, Y and Z are defined above, L is a neutral Lewis base or a donor ligand, r is 0 - 3, and Q is a non-coordinating or weakly coordinating anionic group. L, the optional neutral Lewis base, is conventional and well known. Examples of neutral Lewis bases which L represents include an aliphatic or cyclic ether such as a dialkyl ether containing 2 to about 12 carbon atoms (e.g., tetrahydrofuran), pyridines (e.g., lutidine), and phosphines (e.g., tricyclohexylphosphine). L also may be a species which can act as a donor to the cationic Group 13 metal through coordination of a π -bond, (e.g., benzene or toluene) or even a σ -bond (e.g., H-SiEt₃). Examples of such novel σ -donors are well-known and have been reviewed (see Crabtree, R.H.; *Ang. Chem., Intl. Ed. Engl.*, 1993, 32, 789-805). L also may be a neutral or cationic Group 13 metal species such as [MeC(NⁱPr)₂]AlMe₂, AlMe₃, AlCl₃ or 20 [[MeC(NⁱPr)₂]AlMe]⁺ which coordinates to the cation through a bridging group. In the latter case, dimeric dicationic species can result such as that depicted below (related oligomers are readily envisioned).



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The presence of such neutral coordinating ligands L is not critical, and they may and may not be present as deemed appropriate in any particular reaction.

The Q moiety represents the non-coordinating or weakly coordinating counterbalancing anion. In particular, it represents a compatible, non-coordinating anion containing a single coordination complex comprising a charge-bearing metal or metalloid core which is relatively large (bulky), capable of stabilizing the active catalyst species and being sufficiently labile to be displaced by olefinic, di-olefinic or acetylenically unsaturated substrates, or other neutral Lewis bases or donor groups, such as ethers, nitriles and the like. Polyhedral borane anions, carborane anions and metallocarborane anions are also useful non-coordinating or weakly coordinating counterbalancing anions.

The key to proper anion design requires that the anionic complex is labile and stable toward reactions in the final catalyst species. Anions which are stable toward reactions with water or Bronsted acids and which do not have acidic protons located on the exterior of the anion (i.e. anionic complexes which do not react with strong acids or bases) possess the stability necessary to qualify as a stable anion for the catalyst system. The properties of the anion which are important for maximum lability include overall size, and shape (i.e. large radius of curvature), and nucleophilicity.

Using these guidelines one can use the chemical literature to choose non-coordinating anions which can serve as components in the catalyst system. In general, suitable anions for the second component may be any stable and bulky anionic complex having the following molecular attributes: (1) the anion should have a molecular diameter about or greater than 4 angstroms; (2) the anion should form stable salts with reducible Lewis Acids and protonated Lewis bases; (3) the negative charge on the anion should be delocalized over the framework of the anion or be localized within the

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core of the anion; (4) the anion should be a relatively poor nucleophile; and (5) the anion should not be a powerful reducing or oxidizing agent. Anions meeting these criteria, e.g., polynuclear boranes, carboranes, metallacarboranes, polyoxoanions and anionic coordination complexes, are well described in the chemical literature.

Illustrative, but not limiting examples of non-coordinating or weakly coordinating counterbalancing anions represented by Q, are tetra(phenyl)borate, tetra(p-tolyl)borate, tetra(pentafluorophenyl)borate, tetra(3,5-bis-trifluoromethyl-phenyl)borate, $C_2B_9H_{12}^-$, $CB_{11}H_{12}^-$, $B_{12}H_{12}^{2-}$, and $(C_2B_9H_{11})_2Co^-$. Triarylborates such as methyl[tris(pentafluorophenyl)]borate and methyl(tris[3,5-bis(trifluoromethyl)phenyl])borate are also weakly coordinating anions formed by the abstraction of a methyl group from a Group 13 metal by the neutral triarylboron derivatives. Related derivatives in which one group on a boron- or aluminum-ate anion (Q) is derived from a Group 13 catalyst precursor by an abstraction reaction with a boron or aluminum Lewis acid can be envisioned. For instance, the reaction of methyl-alumoxane with dimethylaluminum-(N,N'-diisopropylpivamidinate) may yield a reactive cationic aluminum catalyst associated with a methyl-alumoxanate anion.

As earlier stated, generally, these anions are labile and can be displaced by an olefin, di-olefin or acetylenically unsaturated monomer, have a molecular diameter about or greater than 4 angstroms, form stable salts with reducible Lewis acids and protonated Lewis bases, have a negative charge delocalized over the framework on the anion of which the core thereof is not a reducing or oxidizing agent, and are relatively poor nucleophiles. For other examples of counterbalancing, non-coordinating or weakly coordinating anions, see Strauss, S. H.; *Chemical Reviews*, 1993, 93, 927-942.

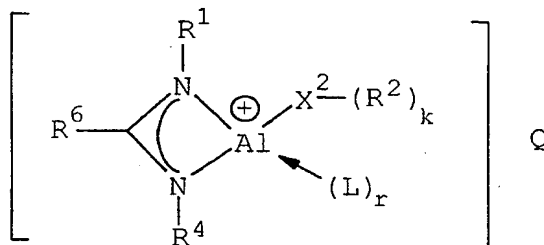
Q preferably represents tetrakis(penta-

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fluorophenyl)boronate or tetrakis[bis(3,5-trifluoromethylphenyl)]boronate.

A preferred embodiment of the complexes of formula (III) are aluminum amidinate compounds having the

5 formula:



wherein R^1 , R^4 , and R^6 are selected from the group consisting of C_1 to C_{50} alkyl, aryl or silyl, $-X^2--(R^2)_k$ is selected from the group consisting of hydrogen, chloride, methyl, ethyl, isobutyl, neopentyl, and benzyl; L is a labile Lewis base or donor ligand or a neutral or cationic aluminum species capable of coordination; and Q is a counterbalancing non-coordinating or weakly coordinating anion.

15 The cationic Group 13 complexes may be prepared by reacting a neutral precursor complex of the type $[(R^1)_jX-Z-Y(R^4)_n]M[X^2(R^2)_k][X^3(R^3)_m]$, where M, R^1 , R^2 , R^3 , R^4 , X^2 , X^3 , k, m, n, and j are as defined above, with an activator capable of abstracting an $-X^3--(R^3)_m$ group from the precursor complex or of cleaving one $M-X^3$ bond of the precursor complex. Suitable activators are those described as component (3) activators in the first and second embodiments above. The syntheses of these catalyst compounds is particularly straightforward and ideally carried out using a high vacuum line and inert atmosphere techniques in the presence of solvents, as presented in the examples. These are illustrative and not intended to be limiting of the invention.

25 The novel catalyst compositions disclosed herein are useful in effecting the polymerization of unsaturated

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compounds such as α -olefins, cyclic olefins, dienes, alkynes, and vinyl aromatic monomers. Preferred monomers are α -olefins containing from 2 to about 8 carbon atoms. Homopolymers preferably are prepared from a C_2 - C_8 α -olefin.

- 5 Copolymers preferably are produced from ethylene and a C_3 - C_8 α -olefin, or propylene and ethylene or another C_4 - C_8 α -olefin. Terpolymers preferably are produced from ethylene and/or propylene and 1 or 2 other C_2 - C_8 α -olefins.

- 10 Polymerizations may be conducted by solution, slurry or gas-phase techniques, generally at a temperature in the range of about 0 to 160°C or even higher, and under atmospheric, subatmospheric or superatmospheric pressure conditions. Conventional polymerization adjuvants such as hydrogen may be employed if desired. It is generally
15 preferred to use the catalyst compositions at a concentration such as to provide about 0.00001 to 0.05 weight percent, most preferably about 0.0001 to 0.005 weight percent of Group 13 metal catalyst.

- A solution polymerization process can utilize sub- or
20 super-atmospheric pressure and temperatures in the range of about 40 to 150°C. Catalyst precursor, co-catalysts, and polymerization additives are dissolved in a liquid medium to which ethylene and/or another unsaturated monomer, and hydrogen are added. The liquid employed as polymerization
25 medium can be an inert alkane or cycloalkane, such as butane, pentane, hexane or cyclohexane, or an inert, aromatic hydrocarbon, such as toluene, ethylbenzene or xylene. The medium employed should be liquid under the conditions of the polymerization and relatively inert.
30 Preferably, hexane or toluene is employed.

- A slurry polymerization process is practiced under similar conditions of pressure and temperature with a suspension of solid, particulate polymer formed in the polymerization medium to which ethylene and/or another
35 unsaturated monomer, hydrogen and catalyst are added. The

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liquids employed are similar to those referred to above for solution polymerization with hexane or toluene typically preferred.

Both solution and slurry polymerization may be performed in a bulk phase where the monomer serves as the liquid reaction medium.

Gas-phase polymerization processes utilize superatmospheric pressure and temperature in the range of about 50 to 120°C. Gas-phase polymerization can be performed in a stirred or fluidized bed of catalyst and product particles in a pressure vessel adapted to permit the separation of product particles from unreacted gases. It may be advantageous to use a supported catalyst prepared by depositing catalyst and co-catalyst components on a support material such as alumina, silica, or magnesium chloride. Thermostated ethylene, comonomer, hydrogen and an inert diluent gas such as nitrogen can be introduced or recirculated so as to maintain the particles at a temperature of 50 to 120°C. Trialkylaluminum may be added as needed as scavenger of water, oxygen and other adventitious impurities. Polymer product can be withdrawn continuously or semicontinuously at a rate such as to maintain a constant product inventory in the reactor. After polymerization and deactivation of the catalyst, the product polymer can be recovered by any suitable means. In commercial practice, the polymer product can be recovered directly from the gas phase reactor, freed of residual monomer with a nitrogen purge, and used with or without further deactivation or catalyst removal. The polymer obtained can be extruded into water and cut into pellets or other suitable comminuted shapes. Pigments, antioxidants and other additives, as is known in the art, may be added to the polymer.

The molecular weight of the polymer products obtained from the polymerization processes using the novel catalyst compositions can vary over a wide range, such as low as 500

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up to 2,000,000 grams per mole or higher, preferably about 1,000 to 500,000 grams per mole. It is highly desirable to have for many applications, such as extrusion and molding processes, polyethylenes which have a broad molecular weight distribution of the unimodal and/or the multimodal type. Such polyethylenes exhibit excellent processability, i.e., they can be processed at a faster throughput rate with lower energy requirements and at the same time such polymers would evidence reduced melt flow perturbations.

10

EXAMPLES

In the following examples all procedures were performed on a high-vacuum line or in a glove box under a purified N₂ atmosphere. Solvents were distilled from Na/benzophenone ketyl, except for chlorinated solvents, which were distilled from activated molecular sieves (3Å) or CaH₂.

N-isopropyl-2-(isopropylamino)troponimine ((ⁱPr)₂ATI}H), (AdNH)₂C=S (Ad = adamantyl), (ArNH)₂C=S (Ar = 2,6-ⁱPrC₆H₃), AdN=C=NAd, ArN=C=NAr, HC(CMeNAr)₂H, and Li[^tBuC(NⁱPr)₂] and Li[^tBuC(NCy)₂], were prepared by literature methods, see Dias, H.V.R.; Jin, W.; Ratcliff, R.E. *Inorg. Chem.* **1995**, 34, 6100; Stetter, H.; Wulff, C. *Chem. Ber.* **1962**, 95, 2302; Ogawa, K; Akazawa, M. *Japanese Pat. Appl.* JP 91-164070 910410; Ogawa, K; Akazawa, M. *Japanese Pat. Appl.* JP 91-208987 910517; Feldman, J.; McLain, S. J.; Parthasarathy, A.; Marshall, W. J.; Calabrese, J.C.; Arthur, S.D. *Organometallics* **1997**, 16, 1514; Coles, M. P.; Swenson, D. C.; Jordan, R. F.; Young Jr., V.A. *Organometallics* **1997**, 16, 5183, which are incorporated by reference.

HC(CMeNAr')₂H (Ar' = 2-^tBuC₆H₄) and HC(CMeN^tBu)(CMeO)H were prepared in an analogous fashion to HC(CMeNAr)₂H using 2-^tBuC₆H₄NH₂ and ^tBuNH₂ respectively.

NMR spectra were recorded on a Bruker AMX 360 spectrometer in sealed or Teflon-valved tubes at ambient probe temperature unless otherwise indicated. ¹H and ¹³C

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chemical shifts are reported versus SiMe₄ and were determined by reference to the residual ¹H and ¹³C solvent peaks. Coupling constants are reported in Hz. ¹³C NMR spectra of ionic compounds containing B(C₆F₅)₄⁻ counterions also contain anion resonances which are not listed in some cases: δ 149 (d, ¹J_{CF}=242), 139 (d, ¹J_{CF}=246), 137 (d, ¹J_{CF}=246), 125 (br, ipso-B(C₆F₅)₄⁻).

Mass spectra were obtained using the Direct Insertion Probe (DIP) method, on a VG Analytical Trio I instrument operating at 70 eV. Elemental analyses were performed by Desert Analytics Laboratory.

EXAMPLE 1

{MeC(NⁱPr)₂}AlMe₂. A solution of 1,3-diisopropylcarbodiimide (2.00 g, 10.7 mmol) in hexane (25 mL) was added dropwise via pipette to a rapidly stirred solution of AlMe₃ (1.06 mL, 11.0 mmol) in hexane (10 mL). An exothermic reaction was observed. The reaction mixture was stirred at room temperature for 18 h, after which time the volatiles were removed under vacuum affording pure {MeC(NⁱPr)₂}AlMe₂ as a pale yellow liquid (2.30 g, 71%). ¹H NMR (CD₂Cl₂): δ 3.50 (sept, ³J_{HH}=6.3 Hz, 2H, CHMe₂), 1.94 (s, 3H, CMe), 1.05 (d, ³J_{HH}=6.1 Hz, 12H, CHMe₂), -0.82 (s, 6H, AlMe₂). ¹³C NMR (CD₂Cl₂): δ 172.5 (s, CMe), 45.3 (d, ¹J_{CH}=132.2 Hz, CHMe₂), 25.3 (q, ¹J_{CH}=125.6 Hz, CHMe₂), 11.1 (q, ¹J_{CH}=128.3 Hz, CMe), -9.94 (br q, ¹J_{CH}=114.1 Hz, AlMe₂). **Anal.** Calcd for C₁₀H₂₃N₂Al: C, 60.57; H, 11.69; N, 14.13. Found: C, 60.41; H, 11.96; N, 14.50.

EXAMPLE 2

{MeC(NCy)₂}AlMe₂. A solution of 1,3-dicyclohexylcarbodiimide (5.00 g, 24.2 mmol) in hexane (40 mL) was added slowly to a solution of AlMe₃ (2.40 mL, 25.0 mmol) in

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hexane (15 mL). The solution was stirred for 15 h and the volatiles were removed under vacuum yielding a pale yellow liquid that crystallized upon standing to afford pure $\{\text{MeC}(\text{NCy})_2\}\text{AlMe}_2$ as off-white crystals. (6.49 g, 93%). ^1H

5 **NMR** (CD_2Cl_2): δ 3.10 (m, 2H, Cy), 1.92 (s, 3H, CMe), 1.69 (m, 8H, Cy), 1.56 (m, 2H, Cy), 1.35-1.06 (m, 8H+2H, Cy), -0.82 (s, 6H, AlMe_2). ^{13}C **NMR** (CD_2Cl_2): δ 172.4 (s, CMe), 53.0 (d, $^1J_{\text{CH}}=131.4$ Hz, Cy- C_1), 36.0 (t, $^1J_{\text{CH}}=126.5$ Hz, Cy), 26.1 (t, $^1J_{\text{CH}}=125.8$ Hz, Cy), 25.4 (t, $^1J_{\text{CH}}=126.9$ Hz, Cy), 11.2 (q, $^1J_{\text{CH}}=128.0$ Hz, CMe), -9.78 (br q), $^1J_{\text{CH}}=112.6$ Hz, AlMe_2).
10 **Anal.** Calcd for $\text{C}_{16}\text{H}_{31}\text{N}_2\text{Al}$: C, 69.02; H, 11.22; N, 10.06. Found: C, 68.88; H, 10.44; N, 10.15. **Mass Spec.** (EI, m/z): 263 $[\text{M}]^+$.

15

EXAMPLE 3

$\text{Li}[\text{tBuC}(\text{N}^i\text{Pr})_2]$. A solution of 1,3-diisopropylcarbodiimide (5.00 g, 39.6 mmol) in Et_2O (50 mL) was cooled to 0°C . tBuLi (23.30 mL of a 1.7 M solution in pentane, 39.6 mmol) was added dropwise via syringe and the mixture was
20 allowed to warm to room temperature. After 30 min the solvent was removed under vacuum affording a yellow oily solid which was dried under vacuum (18 h, 23°C) to give a pale yellow solid. Trituration with hexane gave
25 $\text{Li}[\text{tBuC}(\text{N}^i\text{Pr})_2]$ as an off-white powder (4.56 g, 61%). ^1H **NMR** ($\text{THF}-d_8$): δ 3.84 (sept, $^3J_{\text{HH}}=5.7$ Hz, 2H, CHMe_2), 1.13 (s, 9H, CMe_3), 0.96 (d, $^3J_{\text{HH}}=6.1$ Hz, 12H, CHMe_2). ^{13}C **NMR** ($\text{THF}-d_8$): δ 168.5 (s, CCMe_3), 46.6 (d, $^1J_{\text{CH}}=122.3$ Hz, CHMe_2), 39.4 (s, CMe_3), 31.0 (q, $^1J_{\text{CH}}=116.1$ Hz, CHMe_2), 26.3
30 (q, $^1J_{\text{CH}}=116.1$ Hz, CMe_3).

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EXAMPLE 4

$\text{Li}[\text{tBuC}(\text{NCy})_2]$. A solution of 1,3-dicyclohexylcarbodiimide (5.00 g, 24.2 mmol) in Et_2O (50 mL) was cooled to 0°C. tBuLi (14.3 mL of a 1.7 M solution in pentane, 24.2 mmol) was added via syringe and the mixture was allowed to warm to room temperature. After 30 min the volatile components were removed under vacuum affording a yellow oily solid which was dried overnight under vacuum to yield a pale yellow powder. Trituration of this solid with pentane gave $\text{Li}[\text{tBuC}(\text{NCy})_2]$ as a pale yellow powder (4.91 g, 75%). ^1H NMR ($\text{THF}-d_8$): δ 3.50 (m, 2H, Cy), 1.81-0.93 (m, 20H, Cy), 1.10 (s, 9H, CMe_3). ^{13}C NMR ($\text{THF}-d_8$): δ 168.3 (s, CCMe_3), 55.9 (d, $^1J_{\text{CH}}=119.8$ Hz, Cy- C_1), 39.5 (s, CMe_3), 37.7 (t, $^1J_{\text{CH}}=118.9$ Hz, Cy), 31.1 (q, $^1J_{\text{CH}}=117.7$ Hz, CMe_3), 28.2 (t, partially obscured, Cy), 26.8 (t, $^1J_{\text{CH}}=119.4$ Hz, Cy).

EXAMPLE 5

$\{\text{tBuC}(\text{N}^i\text{Pr})_2\}\text{AlCl}_2$. A solution of AlCl_3 (1.40 g, 10.5 mmol) in Et_2O (30 mL) was cooled to -78°C and added dropwise to a slurry of $\text{Li}[\text{tBuC}(\text{N}^i\text{Pr})_2]$ (2.00 g, 10.5 mmol) in Et_2O (50 mL) which was also at -78°C. The mixture was warmed to room temperature and stirred for 16 h, affording a slurry of a white solid in a yellow solution. The volatiles were removed under vacuum and the product was extracted from the LiCl with pentane. Concentration of the pentane extract and cooling to 0°C afforded pure $\{\text{tBuC}(\text{N}^i\text{Pr})_2\}\text{AlCl}_2$ as opaque white crystals which were collected by filtration (2.01 g, 68%). ^1H NMR (CD_2Cl_2): δ 4.12 (br sept, $^3J_{\text{HH}}=5.9$ Hz, 2H, CHMe_2), 1.43 (s, 9H, CMe_3), 1.18 (d, $^3J_{\text{HH}}=6.2$ Hz, 12H, CHMe_2). ^{13}C NMR (CD_2Cl_2): δ 184.3 (s, CCMe_3), 46.6 (d, $^1J_{\text{CH}}=135.7$ Hz,

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CHMe₂), 40.1 (s, CMe₃), 29.2 (q, ¹J_{CH}=125.7 Hz, CMe₃), 25.9 (q, ¹J_{CH}=124.1 Hz, CHMe₂). **Anal.** Calcd for C₁₁H₂₃N₂AlCl₂: C, 46.98; H, 8.24; N, 9.96. Found: C, 46.84; H, 8.12; N, 9.85. **Mass Spec.** (EI, m/z, ³⁵Cl): 265 [M]⁺.

5

EXAMPLE 6

{^tBuC(NCy)₂}AlCl₂. A solution of AlCl₃ (0.99 g, 7.4 mmol) in Et₂O (25 mL) was added dropwise to a slurry of
10 Li[^tBuC(NCy)₂] (2.00 g, 7.4 mmol) in Et₂O (50 mL) at -78°C. The mixture was warmed to room temperature and stirred for 18 h, affording a slurry of a white precipitate in a yellow solution. The volatiles were removed under vacuum and the product was extracted from the LiCl with toluene.
15 Concentration of the toluene extract and cooling to 0°C afforded pure {^tBu(NCy)₂}AlCl₂ as colorless crystals which were collected by filtration (1.84 g, 69%). ¹H NMR (CD₂Cl₂): δ 3.62 (br m, 2H, Cy), 1.41 (s, 9H, CMe₃), 1.91-1.71 (m, 4H, Cy), 1.62 (m, 2H, Cy), 1.30-1.09 (m, 8H+2H, Cy). ¹³C NMR (CD₂Cl₂): δ 184.4 (s, CCMe₃), 54.6 (d, ¹J_{CH}=138.7 Hz, Cy-C₁),
20 40.1 (s, CMe₃), 36.9 (t, ¹J_{CH}=127.9 Hz, Cy), 29.3 (q, ¹J_{CH}=127.7 Hz, CMe₃), 25.7 (t, ¹J_{CH}=125.7 Hz, Cy), 25.6 (t, ¹J_{CH}=125.7 Hz, Cy). **Anal.** Calcd for C₁₇H₃₁N₂AlCl₂: C, 56.51; H, 8.65; N, 7.75. Found: C, 56.22; H, 8.70; N, 7.67. **Mass Spec.**
25 (EI, m/z, ³⁵Cl): 360 [M]⁺.

EXAMPLE 7

{^tBuC(NⁱPr)₂}AlMe₂. A solution of AlMe₂Cl (0.25 mL, 2.7
30 mmol) in Et₂O (25 mL) was added dropwise to a slurry of Li[^tBuC(NⁱPr)₂] (0.50 g, 2.6 mmol) in Et₂O (30 mL) at -78°C. The reaction mixture was allowed to warm slowly to room temperature and was stirred for 18 h. The volatiles were

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removed under vacuum and the residue was extracted with pentane. The extract was evaporated to dryness under vacuum yielding $\{^t\text{BuC}(\text{N}^i\text{Pr})_2\}\text{AlMe}_2$ as a pale yellow solid (0.57 g, 87%). ^1H NMR (CD_2Cl_2): δ 4.07 (sept, $^3J_{\text{HH}}=6.2$ Hz, 2H, CHMe_2), 1.38 (s, 9H, CMe_3), 1.06 (d, $^3J_{\text{HH}}=6.1$ Hz, 12H, CHMe_2), -0.81 (s, 6H, AlMe_2). ^{13}C NMR (CD_2Cl_2): δ 178.4 (s, CCMe_3), 45.8 (d, $^1J_{\text{CH}}=135.3$ Hz, CHMe_2), 40.0 (s, CMe_3), 29.7 (q, $^1J_{\text{CH}}=127.0$ Hz, CHMe_2), 26.3 (q, $^1J_{\text{CH}}=125.5$ Hz, CMe_3), -9.06 (br q, $^1J_{\text{CH}}=117.7$ Hz, AlMe_2). **Anal.** Calcd for $\text{C}_{13}\text{H}_{29}\text{N}_2\text{Al}$: C, 64.96; H, 12.16; N, 11.65. Found: C, 64.46; H, 11.90; N, 11.90. **Mass Spec.** (EI, m/z): 240 $[\text{M}]^+$, 225 $[\text{M}-\text{CH}_3]^+$.

EXAMPLE 8

$\{^t\text{BuC}(\text{NCy})_2\}\text{AlMe}_2$. A solution of AlMe_2Cl (0.71 mL, 7.7 mmol) in Et_2O (30 mL) was added dropwise to a slurry of $\text{Li}[^t\text{BuC}(\text{NCy})_2]$ (2.00 g, 7.4 mmol) in Et_2O (40 mL) at -78°C . The mixture was allowed to warm to room temperature and was stirred for 15 h. The volatiles were removed under vacuum and the residue was extracted with pentane (3x15 mL). The extract was concentrated to 30 mL and maintained at room temperature affording $\{^t\text{BuC}(\text{NCy})_2\}\text{AlMe}_2$ (2.00 g, 83%) as large colorless crystals which were collected by filtration. ^1H NMR (CD_2Cl_2): δ 3.56 (m, 2H, Cy), 1.80-1.69 (m, 8H, Cy), 1.61-1.57 (m, 2H, Cy), 1.36 (s, 9H, CMe_3), 1.27-1.03 (m, 8H+2H, Cy), -0.83 (s, 6H, AlMe_2). ^{13}C NMR (CD_2Cl_2): δ 178.5 (s, CCMe_3), 54.2 (d, $^1J_{\text{CH}}=125.9$ Hz, $\text{Cy}-\text{C}_1$), 39.9 (s, CMe_3), 37.3 (t, $^1J_{\text{CH}}=119.3$ Hz, Cy), 29.7 (q, $^1J_{\text{CH}}=117.3$ Hz, CMe_3), 26.1 (t, $^1J_{\text{CH}}=119.3$ Hz, Cy), 26.0 (t, $^1J_{\text{CH}}=119.3$ Hz, Cy), -9.1 (br q, $^1J_{\text{CH}}=103.9$ Hz, AlMe_2). **Anal.** Calcd for $\text{C}_{19}\text{H}_{37}\text{N}_2\text{Al}$: C, 71.20; H, 11.64; N, 8.74. Found: C, 71.18; H, 11.88; N,

8.73. **Mass Spec.** (EI, m/z): 320 $[M]^+$, 305 $[M-CH_3]^+$.

EXAMPLE 9

5 $\{^t\text{BuC}(\text{N}^i\text{Pr})_2\}\text{Al}(\text{CH}_2\text{Ph})_2$. A solution of
 $\{^t\text{BuC}(\text{N}^i\text{Pr})_2\}\text{AlCl}_2$ (0.50 g, 1.8 mmol) in Et_2O (25 mL) was
 cooled to -78°C and PhCH_2MgCl (3.56 mL of a 1.0 M solution
 in Et_2O , 3.6 mmol) was added dropwise via syringe. The
 reaction mixture was allowed to warm to room temperature and
10 was stirred for 15 h. The volatiles were removed under
 vacuum and the residue was extracted with pentane. The
 extract was evaporated to dryness under vacuum affording
 pure $\{^t\text{BuC}(\text{N}^i\text{Pr})_2\}\text{Al}(\text{CH}_2\text{Ph})_2$ as a viscous oil (0.55 g, 79%)
 that was induced to solidify through storage at -40°C . **^1H**
15 **NMR** (CD_2Cl_2): δ 7.11 (t, $^3J_{\text{HH}}=7.6$ Hz, 4H, *m*-Ph), 7.02
 (d, $^3J_{\text{HH}}=6.9$ Hz, 4H, *o*-Ph), 6.88 (t, $^3J_{\text{HH}}=7.3$ Hz, 2H, *p*-Ph), 4.00
 (sept, $^3J_{\text{HH}}=6.2$ Hz, 2H, CHMe_2), 1.75 (s, 4H, CH_2Ph), 1.34
 (s, 9H, CMe_3), 0.94 (d, $^3J_{\text{HH}}=6.2$ Hz, 12H, CHMe_2). **^{13}C NMR**
 (CD_2Cl_2): δ 180.8 (s, CCMe_3), 146.8 (s, *ipso*-Ph), 128.2
20 (d, $^1J_{\text{CH}}=155.8$ Hz, *o*- or *m*-Ph), 127.5 (d, $^1J_{\text{CH}}=149.4$ Hz, *o*- or
 m-Ph), 121.7 (d, $^1J_{\text{CH}}=148.5$ Hz, *p*-Ph), 45.6 (d, $^1J_{\text{CH}}=128.9$
 Hz, CHMe_2), 40.1 (s, CMe_3), 29.6 (q, $^1J_{\text{CH}}=119.0$ Hz, CMe_3), 26.3
 (q, $^1J_{\text{CH}}=116.4$ Hz, CHMe_2), 21.4 (br t, $^1J_{\text{CH}}=108.9$ Hz, CH_2Ph).
 Anal. Calcd for $\text{C}_{25}\text{H}_{37}\text{N}_2\text{Al}$: C, 76.49; H, 9.50; N, 7.14.
25 Found: C, 75.05; H, 9.63; N, 6.89. **Mass Spec.** (EI, m/z): 301
 $[M-\text{CH}_2\text{Ph}]^+$.

EXAMPLE 10

30 $\{^t\text{BuC}(\text{NCy})_2\}\text{Al}(\text{CH}_2\text{Ph})_2$. A solution of
 $\{^t\text{BuC}(\text{NCy})_2\}\text{AlCl}_2$ (0.50 g, 1.4 mmol) in Et_2O (20 mL) was
 cooled to -78°C and PhCH_2MgCl (2.76 mL of a 1.0 M solution

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in Et₂O, 2.8 mmol) was added dropwise by syringe. The mixture was allowed to warm slowly to room temperature and was stirred for 15 h. The volatiles were removed under vacuum and the residue was extracted with pentane. The extract was evaporated under vacuum affording pure {^tBuC(NCy)₂}Al(CH₂Ph)₂ as a viscous white oil. (0.57 g, 87%). ¹H NMR (CD₂Cl₂): δ 7.08 (t, ³J_{HH}=7.6 Hz, 4H, *m*-Ph), 6.98 (d, ³J_{HH}=6.9 Hz, 4H, *o*-Ph), 6.84 (t, ³J_{HH}=7.3 Hz, 2H, *p*-Ph), 3.44 (m, 2H, Cy), 1.69 (s, 4H, CH₂Ph), 1.63-1.51 (m, 4H+2H, Cy), 1.27 (s, 9H, CMe₃), 1.21-0.78 (m, 14H, Cy). ¹³C NMR (CD₂Cl₂): δ 180.8 (s, CCMe₃), 146.9 (s, *ipso*-Ph), 126.2 (d, ¹J_{CH}=155.8 Hz, *o*- or *m*-Ph), 127.5 (d, ¹J_{CH}=147.6 Hz, *o*- or *m*-Ph), 121.6 (d, ¹J_{CH}=151.3 Hz, *p*-Ph), 54.0 (d, partially obscured, Cy-C₁), 40.0 (s, CMe₃), 37.1 (t, ¹J_{CH}=117.7 Hz, Cy), 29.6 (q, ¹J_{CH}=117.3 Hz, CMe₃), 25.9 (t, ¹J_{CH}=118.2 Hz, Cy), 25.7 (t, ¹J_{CH}=118.2 Hz, Cy), 21.4 (t, ¹J_{CH}=108.7 Hz, CH₂Ph). **Anal.** Calcd for C₃₁H₄₅N₂Al: C, 78.77; H, 9.60; N, 5.93. Found: C, 78.62; H, 9.58; N, 5.83.

20

EXAMPLE 11

{^tBuC(N^{*i*}Pr)₂}Al(CH₂CMe₃)₂. {^tBuC(N^{*i*}Pr)₂}AlCl₂ (0.50 g, 1.8 mmol) and LiCH₂CMe₃ (0.28 g, 3.6 mmol) were mixed as solids in the glove box. Et₂O (40 mL) was added at -78°C and the mixture was allowed to warm slowly to room temperature, affording a colorless solution and a white precipitate. The mixture was stirred for 18 h and the volatiles were removed under vacuum. The residue was extracted with pentane (3 x 10 mL). The extract was taken to dryness under vacuum affording {^tBuC(N^{*i*}Pr)₂}Al(CH₂CMe₃)₂ as a white solid (0.58 g, 93%). ¹H NMR (CD₂Cl₂): δ 4.13

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(sept, $^3J_{HH}=6.2$ Hz, CHMe_2), 1.39 (s, 9H, CMe_3), 1.15 (d, $^3J_{HH}=6.3$ Hz, CHMe_2), 0.99 (s, 18H, CH_2CMe_3), 0.27 (s, 4H, CH_2CMe_3). ^{13}C NMR (CD_2Cl_2): δ 179.7 (s, CCMe_3), 46.1 (d, $^1J_{CH}=121.0$ Hz, CHMe_2), 40.1 (s, CMe_3), 35.2 (q, $^1J_{CH}=112.2$ Hz, CH_2CMe_3), 32.1 (br t, partially obscured, CH_2CMe_3), 31.6 (s, CH_2CMe_3), 29.8 (q, $^1J_{CH}=121.2$ Hz, CMe_3), 26.6 (q, $^1J_{CH}=117.9$ Hz, CHMe_2). **Anal.** Calcd for $\text{C}_{21}\text{H}_{45}\text{N}_2\text{Al}$: C, 71.54; H, 12.86; N, 7.95. Found: C, 70.46; H, 12.82; N, 7.72. **Mass Spec.** (EI, m/z): 281 $[\text{M}-\text{CH}_2\text{CMe}_3]^+$.

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EXAMPLE 12

{ $^t\text{BuC}(\text{NCy})_2$ }Al(CH_2CMe_3) $_2$. A solution of $\text{LiCH}_2\text{CMe}_3$ (0.43 g, 5.5 mmol) in Et_2O (20 mL) was added dropwise at -78°C to an Et_2O solution (30 mL) of { $^t\text{BuC}(\text{NCy})_2$ }AlCl $_2$ (1.00 g, 2.8 mmol). The reaction mixture was allowed to warm slowly to room temperature and was stirred for 15 h. The volatiles were removed under vacuum and the residue was extracted with pentane. The extract was evaporated to dryness under vacuum to afford pure { $^t\text{BuC}(\text{NCy})_2$ }Al(CH_2CMe_3) $_2$ as a white solid material (1.13 g, 94%). ^1H NMR (CD_2Cl_2): δ 3.63 (m, 2H, Cy), 1.86-1.71 (m, 8H, Cy), 1.60 (m, 2H, Cy), 1.36 (s, 9H, CMe_3), 1.30-1.09 (m, 8H+2H, Cy), 0.99 (s, CH_2CMe_3), 0.25 (s, 4H, CH_2CMe_3). ^{13}C NMR (CD_2Cl_2): δ 179.7 (s, CCMe_3), 54.8 (d, $^1J_{CH}=126.8$ Hz, Cy- C_1), 40.0 (s, CMe_3), 37.2 (t, $^1J_{CH}=124.3$ Hz, Cy), 35.2 (q, $^1J_{CH}=117.6$ Hz, CH_2CMe_3), 32.1 (br t, partially obscured, CH_2CMe_3), 31.6 (s, CH_2CMe_3), 29.8 (q, $^1J_{CH}=119.6$ Hz, CMe_3), 26.2 (t, $^1J_{CH}=118.2$ Hz, Cy), 26.1 (t, $^1J_{CH}=118.2$ Hz, Cy). **Anal.** Calcd for $\text{C}_{27}\text{H}_{53}\text{N}_2\text{Al}$: C, 74.95; H, 12.35; N, 6.47. Found: C, 73.87; H, 12.42; N, 6.60. **Mass Spec.** (EI, m/z):

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362 [M-CH₂CMe₃]⁺.EXAMPLE 13

5 [({MeC(NⁱPr)₂ } AlMe)₂ (μ-Me)] [MeB(C₆F₅)₃]. A solution of
 B(C₆F₅)₃ (0.77 g, 1.5 mmol) in CH₂Cl₂ (20 mL) was added to
 {MeC(NⁱPr)₂ } AlMe₂ (0.60 g, 3.0 mmol) also in CH₂Cl₂ (15 mL).
 The reaction mixture was allowed to stir for 30 min at room
 temperature and the volatiles were removed under vacuum
 10 leaving an oily white solid. Trituration with pentane
 afforded [({MeC(NⁱPr)₂ } AlMe)₂ (μ-Me)] [MeB(C₆F₅)₃] as a white
 powder (0.91 g, 83%). ¹H NMR (CD₂Cl₂, 293 K): δ 3.79
 (sept, ³J_{HH}=6.6 Hz, 4H, CHMe₂), 2.31 (s, 6H, CMe), 1.28
 (d, ³J_{HH}=6.5 Hz, 24H, CHMe₂), -0.38 (br s, 9H, AlMe). ¹H NMR
 15 (CD₂Cl₂, 193K): δ 3.79 (br sept, 2H, CHMe₂), 3.67 (br
 sept, 6H, CHMe₂), 2.33 (s, 6H, CMe), 2.15 (s, 6H, CMe), 1.30
 (m, 18H, CHMe₂), 1.18 (m, 12H, CHMe₂), 1.02 (m, 18H, CHMe₂), -0.17
 (s, 6H, AlMe), -0.54 (s, 6H, AlMe), -0.75 (s, 6H, AlMe).
¹¹B NMR (CD₂Cl₂): δ -13.4 (br s, MeB(C₆F₅)₃). ¹³C NMR
 20 (CD₂Cl₂): δ 182.0 (s, CMe), 50.5 (d, ¹J_{CH}=138.9 Hz, CHMe₂),
 23.4 (q, ¹J_{CH}=127.0 Hz, CHMe₂), 17.8 (q, ¹J_{CH}=130.3 Hz, CMe),
 -5.6 (br q, ¹J_{CH}=130.3 Hz, AlMe). **Anal.** Calcd for
 C₃₈H₄₆N₄Al₂BF₁₅: C, 50.23; H, 5.10; N, 6.17. Found: C,
 50.46; H, 4.92; N, 6.09.

25

EXAMPLE 14

 [({MeC(NⁱPr)₂ } AlMe (NMe₂Ph)] [B(C₆F₅)₄]. A CD₂Cl₂
 solution (600 μL) of [HNMe₂Ph][B(C₆F₅)₄] (85.3 mg, 0.11
 30 mmol) was added to a vial containing {MeC(NⁱPr)₂ } AlMe₂ (21.1
 mg, 0.11 mmol). The mixture was transferred to an NMR tube
 and NMR spectra were recorded showing complete conversion to

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[{MeC(NⁱPr)₂}AlMe(NMe₂Ph)][B(C₆F₅)₄]. ¹H NMR (CD₂Cl₂): δ 7.63 (t, ³J_{HH}=7.9 Hz, 2H, *m*-Ph), 7.51 (t, ³J_{HH}=7.3 Hz, 1H, *p*-Ph), 7.47 (d, ³J_{HH}=7.9 Hz, 2H, *o*-Ph), 3.58 (sept, ³J_{HH}=6.4 Hz, 2H, CHMe₂), 3.20 (s, 6H, NMe₂Ph), 2.17 (s, 3H, CMe), 1.03 (d, ³J_{HH}=6.5 Hz, 6H, CHMe₂), 0.92 (d, ³J_{HH}=6.4 Hz, 6H, CHMe₂), -0.30 (s, 3H, AlMe). ¹³C NMR (CD₂Cl₂): δ 182.0 (s, CMe), 143.7 (s, *ipso*-Ph), 131.4 (d, ¹J_{CH}=159.4 Hz, *o*-Ph), 129.8 (d, ¹J_{CH}=164.8 Hz, *p*-Ph), 120.9 (d, ¹J_{CH}=153.1 Hz, *m*-Ph), 46.7 (q, ¹J_{CH}=134.7 Hz, NMe₂), 46.0 (d, ¹J_{CH}=125.2 Hz, CHMe₂), 24.7 (q, ¹J_{CH}=119.7 Hz, CHMe₂), 24.6 (q, ¹J_{CH}=119.7 Hz, CHMe₂), 12.7 (q, ¹J_{CH}=122.6 Hz, CMe), -13.4 (br q, ¹J_{CH}=116.8 Hz, AlMe).

EXAMPLE 15

15 [{MeC(NⁱPr)₂}AlMe(PMe₃)] [MeB(C₆F₅)₃]. A CD₂Cl₂ solution of [{MeC(NⁱPr)₂}AlMe]₂(μ-Me)[MeB(C₆F₅)₃] was cooled in liquid N₂ and PMe₃ (5 equiv) was condensed onto the frozen solution. The mixture was warmed to room temperature and the ¹H NMR spectrum was recorded, showing 20 that complete formation of the trimethylphosphine adduct [{MeC(NⁱPr)₂}AlMe(PMe₃)] [MeB(C₆F₅)₃] and {MeC(NⁱPr)₂}AlMe₂ had occurred. To obtain a sample free from reaction byproducts, the NMR tube was evacuated and pumped on for 18 h. The resulting oily solid was redissolved in CD₂Cl₂ and 25 the NMR spectra was recorded, and showed that only [{MeC(NⁱPr)₂}AlMe(PMe₃)] [MeB(C₆F₅)₃] was present. ¹H NMR (CD₂Cl₂): δ 3.62 (sept, ³J_{HH}=6.3 Hz, 2H, CHMe₂), 2.17 (s, 3H, CMe), 1.52 (d, ²J_{PC}=9.4 Hz, 9H, PMe₃), 1.10 (d, ³J_{HH}=6.3 Hz, 12H, CHMe₂), -0.27 (s, 3H, AlMe). ³¹P NMR (CD₂Cl₂): δ -34.55 30 (s, PMe₃). ¹³C NMR (CD₂Cl₂): δ 180.6 (s, CMe), 45.5

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(d, $^1J_{CH}=131.1$ Hz, CHMe₂), 25.3 (q, $^1J_{CH}=121.0$ Hz, CHMe₂), 12.4 (q, $^1J_{CH}=124.7$ Hz, CMe), 9.1 (dq, $^1J_{PC}=29.6$ Hz, $^1J_{CH}=127.6$ Hz, PMe₃), -12.8 (br q, $^1J_{CH}=109.6$ Hz, AlMe).

5

EXAMPLE 16

[{MeC(NⁱPr)₂}AlMe(PMe₃)] [B(C₆F₅)₄]. A CD₂Cl₂ solution of [{MeC(NⁱPr)₂}AlMe(NMe₂Ph)] [B(C₆F₅)₄] was cooled in liquid N₂ and PMe₃ (5 equiv) was condensed onto the frozen
10 solution. The mixture was warmed to room temperature and the ¹H NMR spectrum was recorded, showing that formation of the trimethylphosphine adduct [{MeC(NⁱPr)₂}AlMe(PMe₃)] [B(C₆F₅)₄] and free NMe₂Ph had occurred. ¹H NMR (CD₂Cl₂): δ 3.62 (sept, $^3J_{HH}=6.3$ Hz, 2H, CHMe₂), 2.17 (s, 3H, CMe), 1.52 (d, $^2J_{PC}=9.4$ Hz, 9H, PMe₃),
15 1.10 (d, $^3J_{HH}=6.3$ Hz, 12H, CHMe₂), -0.27 (s, 3H, AlMe). ³¹P NMR (CD₂Cl₂): δ -34.55 (s, PMe₃). ¹³C NMR (CD₂Cl₂): δ 180.6 (s, CMe), 45.5 (d, $^1J_{CH}=131.1$ Hz, CHMe₂), 25.3 (q, $^1J_{CH}=121.0$ Hz, CHMe₂), 12.4 (q, $^1J_{CH}=124.7$ Hz, CMe), 9.1 (dq, $^1J_{PC}=29.6$ Hz, $^1J_{CH}=127.6$ Hz, PMe₃), -12.8 (br q, $^1J_{CH}=109.6$ Hz, AlMe).
20

Based upon the above synthesis illustration Examples 1-16, it can be seen that the cationic aluminum alkyl complexes are prepared by reacting a neutral precursor complex of the type R²C(NR¹)(NR³)AlX₂, where R¹, R², R³ and
25 X are as defined above, with an activator compound which is capable of abstracting one X- group from the precursor complex or of cleaving one Al-X bond of the precursor complex. Additionally, example 15 shows that the {MeC(NⁱPr)₂}AlMe₂ moiety of [{MeC(NⁱPr)₂}AlMe]₂(μ-Me)[MeB(C₆F₅)₃] can be displaced by the Lewis base PMe₃, and
30 example 16 shows that the NMe₂Ph group of

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[{MeC(NⁱPr)₂}AlMe(NMe₂Ph)][B(C₆F₅)₄] can be displaced by PMe₃.

The following two additional examples illustrate the preparation of base-free cations.

5

EXAMPLE 17

[{^tBuC(NⁱPr)₂}AlMe][MeB(C₆F₅)₃]. A solution of {^tBuC(NⁱPr)₂}AlMe₂ (0.041 g, 0.17 mmol) in toluene (1.5 cm³) was prepared in the dry box. This was added dropwise via pipette to a solution of 1 equiv B(C₆F₅)₃ (0.087 g, 0.17 mmol) also in toluene (2.5 cm³) that was rapidly stirring in an ampoule fitted with a teflon tap. The ampoule was sealed and the mixture was removed from the dry box and stirred on a vacuum line for 30 mins. The volatiles were then removed under reduced pressure, leaving an off-white, oily residue. (CD₂Cl)₂ was added to this residue and the solution transferred to an NMR tube. The ¹H NMR spectrum was recorded immediately and showed complete conversion to the desired base-free cation [{^tBuC(NⁱPr)₂}AlMe][MeB(C₆F₅)₃]. ¹H NMR (CD₂Cl₂): δ 4.12 (sept, ³J_{HH}=6.2 Hz, 2H, CHMe₂), 1.67 (br s, 3H, BCH₃), 1.42 (s, 9H, CMe₃), 1.09 (d, 6H, ³J_{HH}=6.2 Hz, CHMe₂), 0.96 (d, 6H, ³J_{HH}=6.2 Hz, CHMe₂), -0.44 (br s, 3H, AlMe). ¹³C NMR (CD₂Cl)₂: δ 181.3 (s, CCMe₃), 46.0 (d, ¹J_{CH}=132.1 Hz, CHMe₂), 40.1 (s, CMe₃), 29.3 (q, ¹J_{CH}=122.3 Hz, CMe₃), 26.4 (q, ¹J_{CH}=125.3 Hz, CHMe₂), 25.5 (q, ¹J_{CH}=121.2 Hz, CHMe₂), 16.8 (br q, ¹J_{CH}=108.0 Hz, Me-B), -8.7 (br q, ¹J_{CH}=118.1 Hz, AlMe). C₆F₅ resonances were also observed.

30

EXAMPLE 18

([{^tBuC(NCy)₂}AlMe][MeB(C₆F₅)₃]). The product was prepared in an identical manner to that outlined above,

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using 0.033 g $\{^t\text{BuC}(\text{NCy})_2\}\text{AlMe}_2$ (0.10 mmol) and 0.053 g $\text{B}(\text{C}_6\text{F}_5)_3$ (1 equiv, 0.10 mmol). Again 100% conversion to the base-free cation was observed. $^1\text{H NMR}$ $(\text{CD}_2\text{Cl})_2$: δ 3.61 (m, 2H, Cy), 1.83-1.74 (br m, 4H, Cy), 1.66 (br s, 3H, BCH_3),
5 1.55 (br t, 4H, Cy), 1.37 (s, 9H, CMe_3), 1.25-0.98 (m, 8H, Cy), 0.89-0.79 (m, 4H, Cy), -0.46 (s, 3H, AlMe). $^{13}\text{C NMR}$ $(\text{CD}_2\text{Cl})_2$: δ 181.1 (s, CCMe_3), 54.1 (d, $^1J_{\text{CH}}=134.0$ Hz, Cy-C_1),
39.9 (s, CMe_3), 37.5 (t, $^1J_{\text{CH}}=129.0$ Hz, Cy), 36.6 (t, $^1J_{\text{CH}}=126.2$ Hz, Cy), 29.3 (q, $^1J_{\text{CH}}=122.3$ Hz, CMe_3), 25.8
10 (t, $^1J_{\text{CH}}=122.5$ Hz, Cy), 16.8 (br q, B-Me), -8.5 (q, $^1J_{\text{CH}}=114.7$ Hz, AlMe). C_6F_5 resonances were also observed.

EXAMPLE 19

15 Polymerization Procedure for Ethylene

All polymerizations were carried out using transition metal-free conditions, employing glass apparatus and Teflon-coated stirrer bars.

20 In a typical experiment, 0.02 g of $\{^t\text{BuC}(\text{N}^i\text{Pr})_2\}\text{AlMe}_2$ was weighed out into a glass vial in the dry box, and 3 mL of dry toluene was added. 1 equiv of activator, based on the aluminum compound was weighed into a Fisher-Porter bottle and ca. 50 cm^3 of toluene was added. The aluminum
25 complex solution was added dropwise over 2 minutes (using a pipette) to the rapidly stirring activator solution, ensuring efficient mixing of the 2 components, and a constant excess of activator (to limit formation of base adduct species). The apparatus was then removed from the
30 dry box and connected to the polymerization equipment, consisting of an ethylene cylinder, vacuum line and gas purification system. This had been previously evacuated to remove any residual gas from the system. The mixture was allowed to equilibrate at the temperature required for the

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experiment (10-20 minutes) before the introduction of ethylene. The Fisher-Porter bottle was placed under slight vacuum prior to introduction of the ethylene, to reduce the nitrogen content within and maximize ethylene dissolution in the solvent). The polymerization was typically allowed to run for 60 minutes, after which time the ethylene flow to the system was halted. The apparatus was vented in a fume hood and disassembled. 50-80 mL of a mixture of methanol (ca. 150 mL) and conc. HCl (ca. 1.5 mL) was added to the solution to quench the reaction and the precipitate (if any) was collected by filtration. The polymer was then washed with acidified water (ca. 1.5 mL conc. HCl in 100 mL H₂O) to ensure removal of the Al-salts, and dried in a vacuum oven at 60°C for 2-8 hours. The weight was recorded and the activity calculated (see table).

The results of the ethylene polymerizations are summarized in the table below.

Table of Results for Ethylene Polymerization

(neutral precursor complex = {^tBuC(NⁱPr)₂}AlMe₂; ethylene pressure = 2 atm; solvent = toluene)

Run	Activator Compound	Time (mins)	Temp (°C)	Yield PE (g)	Activity*
1	B(C ₆ F ₅) ₃	60	26	0.053	293
2	B(C ₆ F ₅) ₃	60	60	0.115	697
3	B(C ₆ F ₅) ₃	60	85	0.026	162
4	[Ph ₃ C][B(C ₆ F ₅) ₄]	60	26	0.084	530
5	[Ph ₃ C][B(C ₆ F ₅) ₄]	60	60	0.293	1777
6	[Ph ₃ C][B(C ₆ F ₅) ₄]	30**	60	0.266	3183
7	[Ph ₃ C][B(C ₆ F ₅) ₄]	30**	85	0.351	4145

* g PE/mol cat*hr*atm

** = solution stopped stirring due to formation of a precipitate therefore stopped after 30 mins

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EXAMPLES 20-26**Additional Aluminum Amidinate Complexes**EXAMPLE 20

5 $\{^t\text{BuC}(\text{N}^i\text{Pr})_2\}\text{Al}^i\text{Bu}_2$. A solution of $\text{Al}^i\text{Bu}_2\text{Cl}$ (2.50 mL, 13.1 mmol) in Et_2O (40 mL) was added dropwise to a slurry of $\text{Li}[\text{C}(\text{N}^i\text{Pr})_2]$ (2.50 g, 13.1 mmol) in Et_2O (75 mL) at -50
10 °C. The reaction mixture was allowed to warm to room temperature and was stirred for 16 h, resulting in a slurry of a white solid in a yellow solution. The volatiles were removed under vacuum, the crude product was extracted with pentane and the volatiles were removed from the extract
15 under vacuum to afford $\{^t\text{BuC}(\text{N}^i\text{Pr})_2\}\text{Al}^i\text{Bu}_2$ as a yellow liquid. Yield 3.55 g, 83 %. $^1\text{H NMR}$ (CD_2Cl_2): δ 4.09 (sept, $^3\text{J}_{\text{HH}} = 6.2$, 2H, NCHMe_2), 1.84 (m, $^3\text{J}_{\text{HH}} = 6.8$, 2H, CH_2CHMe_2), 1.38 (s, 9H, CMe_3), 1.10 (d, $^3\text{J}_{\text{HH}} = 6.5$, 12H, CHMe_2), 0.92 (d, $^3\text{J}_{\text{HH}} = 6.8$, 12H, CHMe_2), -0.01 (d, $^3\text{J}_{\text{HH}} = 6.8$, 4H, AlCH_2).
20 $^{13}\text{C NMR}$ (CD_2Cl_2): δ 178.6 (s, CCMe_3), 45.6 (d, $^1\text{J}_{\text{CH}} = 135$, NCHMe_2), 40.0 (s, CMe_3), 29.7 (q, $^1\text{J}_{\text{CH}} = 125$, CMe_3), 28.6 (q, $^1\text{J}_{\text{CH}} = 123$, ^iPr or $^i\text{Bu}-\text{CHMe}_2$), 27.0 (d, $^1\text{J}_{\text{CH}} = 120$, CH_2CHMe_2), 26.3 (q, $^1\text{J}_{\text{CH}} = 125$, ^iPr or $^i\text{Bu}-\text{CHMe}_2$), 23.4 (br t, $^1\text{J}_{\text{CH}} = 107$, AlCH_2).

25

EXAMPLE 21

$\{\text{MeC}(\text{NAd})_2\}\text{AlMe}_2$. A solution of AlMe_3 (0.132 g, 1.84 mmol) in hexane (10 mL) was added dropwise to a rapidly
30 stirred solution of 1,3-diadamantylcarbodiimide (0.500 g, 1.61 mmol) in hexane (30 mL). The reaction mixture was stirred at room temperature for 18 h, and the volatiles were removed under vacuum affording pure $\{\text{MeC}(\text{NAd})_2\}\text{AlMe}_2$ as a white solid (0.62 g, 88%). Analytically pure samples were
35 obtained by recrystallization from Et_2O at -30 °C. $^1\text{H NMR}$

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(CD₂Cl₂): δ 2.22 (s, 3H, CMe), 2.03 (br s, 6H, Ad-H γ), 1.79 (br d, $^2J_{HH}$ = 2.88, 12H, Ad-H β), 1.65 (br s, 12H, Ad-H δ), -0.82 (s, 6H, AlMe₂). **¹³C NMR** (CD₂Cl₂): δ 172.6 (s, CMe), 51.5 (s, Ad-C α), 44.6 (t, $^1J_{CH}$ = 129, Ad-C β), 36.8 (t, $^1J_{CH}$ = 126, Ad-C δ), 30.3 (d, $^1J_{CH}$ = 132, Ad-C γ), 19.7 (q, $^1J_{CH}$ = 128, CMe), -9.6 (br q, $^1J_{CH}$ = 112, AlMe₂). **Anal.** Calcd for C₂₄H₃₉AlN₂: C, 75.35; H, 10.27; N, 7.32. Found: C, 74.96; H, 10.35; N, 7.30.

10

EXAMPLE 22

{^tBuC(NAd)₂}AlMe₂. A solution of 1,3-diadamantylcarbodiimide (2.64 g, 8.50 mmol) in Et₂O (80 mL) was cooled to 0 °C. ^tBuLi (5.0 mL of a 1.7 M solution in hexanes, 8.5 mmol) was added slowly by syringe. The resulting mixture was allowed to warm to room temperature and was stirred for 2 h. The mixture was cooled to -78 °C and a solution of AlMe₂Cl (0.79 mL, 8.5 mmol) in Et₂O (30 mL) was added. The resulting solution was allowed to warm to room temperature and was stirred for 18 h. The volatiles were removed under vacuum and the product was extracted from the LiCl with pentane. The pentane extract was concentrated and cooled to -30 °C to afford {^tBuC(NAd)₂}AlMe₂ as white crystals which were isolated by filtration (0.47 g, 13% based on AlMe₂Cl). The low isolated yield is due to the high solubility of the product. **¹H NMR** (CD₂Cl₂): δ 2.05 (br s, 6H, Ad-H γ), 2.02 (s br, 12H, Ad-H β), 1.62 (br s, 12H, Ad-H δ), 1.47 (s, 9H, CMe₃), -0.76 (s, 6H, AlMe₂). **¹³C NMR** (CD₂Cl₂): δ 182.5 (s, CCMe₃), 55.0 (s, Ad-C α), 46.0 (t, $^1J_{CH}$ = 128, Ad-C β), 38.5 (s, CMe₃), 36.6 (t, $^1J_{CH}$ = 126, Ad-C δ), 32.6 (q, $^1J_{CH}$ = 127, CMe₃), 30.7 (d, $^1J_{CH}$ = 133, Ad-C γ), -6.8 (br q, $^1J_{CH}$ = 113, AlMe₂). **Anal.** Calcd for C₂₇H₄₅AlN₂: C, 76.37; H, 10.68;

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N, 6.60. Found: C, 76.43; H, 10.86; N, 6.65. The structure of this compound was confirmed by X-ray crystallography.

5

EXAMPLE 23

{MeC(NAr)₂}AlMe₂ (Ar = 2,6-*i*Pr₂C₆H₃). This compound was prepared by the procedure described for {MeC(NAd)₂}AlMe₂, using 0.525 g 1,3-bis(2,6-diisopropylphenyl)carbodiimide (1.45 mmol) in 40 mL hexane and 0.111 g AlMe₃ (1.53 mmol) in 10 mL hexane. After 18 h the volatiles were removed under vacuum yielding pure {MeC(NAr)₂}AlMe₂ as an off-white solid. (0.491 g, 74%). **¹H NMR** (CD₂Cl₂): δ 7.19 (m, 6H, NAr), 3.35 (sept, ³J_{HH} = 6.8, 4H, CHMe₂), 1.49 (s, 3H, CMe), 1.23 (d, ³J_{HH} = 7.6, 12H, CHMe₂), 1.21 (d, ³J_{HH} = 7.2, 12H, CHMe₂), -0.53 (s, 6H, AlMe₂). **¹³C NMR** (CD₂Cl₂): δ 176.1 (s, CMe), 145.1 (s, Ar-C_{ortho}), 138.4 (s, Ar-C_{ipso}), 126.3 (d, ¹J_{CH} = 160, Ar-C_{para}), 123.8 (d, ¹J_{CH} = 156, Ar-C_{meta}), 28.5 (d, ¹J_{CH} = 126, CHMe₂), 24.7 (q, ¹J_{CH} = 126, CHMe₂), 23.9 (q, ¹J_{CH} = 126, CHMe₂), 14.4 (q, ¹J_{CH} = 129, CMe), -9.9 (q, ¹J_{CH} = 113, AlMe₂).

25

EXAMPLE 24

{^tBuC(NAr)₂}AlCl₂. This compound was prepared by the procedure described for {^tBuC(NAd)₂}AlMe₂, using 2.85 g 1,3-bis(2,6-diisopropylphenyl)carbodiimide (7.86 mmol) in 80 mL Et₂O, 4.6 mL ^tBuLi (1.7 M solution in pentane, 7.9 mmol) and 1.05 g AlCl₃ (7.86 mmol) in 30 mL Et₂O. After 18 h the volatiles were removed under vacuum yielding an oily yellow solid. {^tBuC(NAr)₂}AlCl₂ was extracted from LiCl with pentane and isolated from the extract by crystallization at

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-30 °C. Yield 0.687 g, 17% based on AlCl_3). ^1H NMR (CD_2Cl_2): δ 7.27 (d, $^3J_{\text{HH}} = 6.5$, 1H, Ar), 7.24 (d, $^3J_{\text{HH}} = 6.8$, 1H, Ar), 7.19 (s, 3H, Ar), 7.17 (d, 1H, Ar), 3.41 (sept, $^3J_{\text{HH}} = 6.7$, 4H, CHMe_2), 1.36 (d, $^3J_{\text{HH}} = 6.5$, 12H, CHMe_2), 1.27 (d, $^3J_{\text{HH}} = 6.8$, 12H, CHMe_2), 0.98 (s, 9H, CMe_3). ^{13}C NMR (CD_2Cl_2): δ 187.3 (s, CCMe_3), 145.3 (s, Ar-Cortho), 136.6 (s, Ar-Cipso), 127.4 (d, $^1J_{\text{CH}} = 159$, Ar-Cpara), 124.2 (d, $^1J_{\text{CH}} = 157$, Ar-Cmeta), 42.5 (s, CMe_3), 29.4 (q, $^1J_{\text{CH}} = 128$, CMe_3), 29.1 (d, $^1J_{\text{CH}} = 128$, CHMe_2), 27.3 (q, $^1J_{\text{CH}} = 131$, CHMe_2), 23.0 (q, $^1J_{\text{CH}} = 126$, CHMe_2).
Anal. Calcd for $\text{C}_{29}\text{H}_{43}\text{AlN}_2\text{Cl}_2$: C, 67.30; H, 8.76; N, 5.41. Found: C, 67.03; H, 8.39; N, 5.43.

EXAMPLE 25

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$\{\text{tBuC}(\text{NAr})_2\}\text{AlMe}_2$. This compound was prepared by the procedure described for $\{\text{tBuC}(\text{NAd})_2\}\text{AlMe}_2$, using 2.71 g 1,3-bis(2,6-diisopropylphenyl)carbodiimide (7.48 mmol) in 80 mL Et_2O , 4.4 mL tBuLi (1.7 M solution in pentane, 7.5 mmol) and 0.7 mL AlMe_2Cl (7.48 mmol) in 30 mL Et_2O . After 15 h the volatiles were removed under vacuum yielding an oily red-brown solid. $\{\text{tBuC}(\text{NAr})_2\}\text{AlMe}_2$ was extracted from LiCl with pentane and isolated from the extract by crystallization at -30 °C. Yield 0.726 g, 20% based on AlMe_2Cl . ^1H NMR (CD_2Cl_2): δ 7.18 - 7.12 (m, 6H, Ar), 3.45 (sept, $^3J_{\text{HH}} = 6.8$, 4H, CHMe_2), 1.34 (d, $^3J_{\text{HH}} = 7.2$, 12H, CHMe_2), 1.16 (d, $^3J_{\text{HH}} = 6.8$, 12H, CHMe_2), 0.91 (s, 9H, CMe_3), -0.6 (s, 6H, AlMe_2). ^{13}C NMR (CD_2Cl_2): δ 180.5 (s, CCMe_3), 145.0 (s, Ar-Cortho), 139.6 (s, Ar-Cipso), 125.9 (d, $^1J_{\text{CH}} = 161$, Ar-Cpara), 123.7 (d, $^1J_{\text{CH}} = 156$, Ar-Cmeta), 42.3 (s, CMe_3), 29.7 (q, $^1J_{\text{CH}} =$

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127, CMe₃), 28.7 (d, ¹J_{CH} = 129, CHMe₂), 27.1 (q, ¹J_{CH} = 128, CHMe₂), 22.8 (q, ¹J_{CH} = 127, CHMe₂), -8.6 (br q, ¹J_{CH} = 113.4, AlMe₂). **Anal.** Calcd for C₃₁H₄₉AlN₂: C, 78.10; H, 10.36; N, 5.88. Found: C, 77.61; H, 10.28; N, 5.78. The
5 structure of this compound was confirmed by X-ray crystallography.

EXAMPLE 26

[{^tBuC(NⁱPr)₂}AlⁱBu][B(C₆F₅)₄]. A solution of
10 {^tBuC(NⁱPr)₂}AlⁱBu₂ (0.088 g, 0.27 mmol) in C₆D₆ (0.80 mL) was added to solid [Ph₃C][B(C₆F₅)₄] (0.250 g, 0.27 mmol) in a vial in the dry box. The mixture was transferred to an NMR tube and shaken vigorously for 2 min. Phase separation occurred to give a mixture of an orange oil (lower layer)
15 and a pale yellow supernatant (upper layer). NMR spectra of the orange oily layer were recorded. These spectra established that the oil contains [{^tBuC(NⁱPr)₂}AlⁱBu][B(C₆F₅)₄], Ph₃CH and H₂C=CMe₂. **¹H NMR** (C₆D₆): δ 3.71 (br sept, ¹J_{HH} = 6.0, 2H, NCHMe₂), 1.39
20 (mult, 1H, CH₂CHMe₂), 1.03 (s, 9H, CMe₃), 0.78 (d, ¹J_{HH} = 5.8, 12H, NCHMe₂), 0.70 (d, ¹J_{HH} = 6.5, 6H, CH₂CHMe₂), -0.65 (d, ¹J_{HH} = 7.6, 2H, AlCH₂). **¹³C NMR** (C₆D₆): δ 189.0 (s, CCMe₃), 46.0 (d, ¹J_{CH} = 140, NCHMe₂), 40.1 (s, CMe₃), 28.1 (q, ¹J_{CH} = 130, CH₂CHMe₂), 26.8 (q, ¹J_{CH} = 124, CMe₃), 25.2
25 (q, ¹J_{CH} = 128, NCHMe₂), 24.8 (d, ¹J_{CH} = 127, CH₂CHMe₂), 16.2 (br t, ¹J_{CH} = 118, AlCH₂).

EXAMPLES 27-31**Beta-diketiminato Complexes**EXAMPLE 27

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{HC(CMeNAr)₂}AlMe₂ (Ar = 2,6-*i*PrC₆H₃). A solution of AlMe₃ (0.108 g, 1.48 mmol) in hexanes (15 mL) was added to a rapidly stirred solution of HC(CMeNAr)₂H (0.600 g, 1.43 mmol) in hexanes (60 mL). A gas was evolved. After 15 h the volatiles were removed to afford {HC(CMeNAr)₂}AlMe₂ as a white crystalline solid (yield 0.569 g, 80%). Analytically pure samples were obtained as colorless crystals by recrystallization from a concentrated Et₂O solution at -30°C. ¹H NMR (CD₂Cl₂): δ 7.23 (m, 6H, NAr), 5.20 (s, 1H, CH), 3.25 (sept, ³J_{HH} = 6.8, 4H, CHMe₂), 1.77 (s, 6H, CMe), 1.25 (d, ³J_{HH} = 5.8, 12H, CHMe₂), 1.17 (d, ³J_{HH} = 7.6, 12H, CHMe₂), -0.99 (s, 6H, AlMe₂). ¹³C NMR (CD₂Cl₂): δ 170.1 (s, CMe), 144.7 (s, Ar-C_{ortho}), 141.1 (s, Ar-C_{ipso}), 126.9 (d, ¹J_{CH} = 161, Ar-C_{para}), 124.5 (d, ¹J_{CH} = 155, Ar-C_{meta}), 97.6 (d, ¹J_{CH} = 160, CH), 28.4 (d, ¹J_{CH} = 129, CHMe₂), 25.4 (q, ¹J_{CH} = 127, CHMe₂), 24.7 (q, ¹J_{CH} = 127, CHMe₂), 23.8 (q, ¹J_{CH} = 131, CMe), -10.6 (br q, ¹J_{CH} = 114, AlMe₂). **Anal.** Calcd for C₃₁H₄₇AlN₂: C, 78.44; H, 9.98; N, 5.90. Found: C, 78.58; H, 10.02; N, 5.81. The structure of this compound was confirmed by X-ray crystallography.

EXAMPLE 28

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{HC(CMeNAr)₂}Al^{*i*}Bu₂. This compound was prepared by the procedure described for {HC(CMeNAr)₂}AlMe₂ (Ar = 2,6-*i*PrC₆H₃), using 2.00 g HC(CMeNAr)₂H (4.78 mmol) in 50 mL pentane and 0.680 g Al^{*i*}Bu₂H (4.78 mmol) in 10 mL pentane. A gas was evolved. After 2.5 h the solution was concentrated

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to half volume. Pure $\{\text{HC}(\text{CMeNAr})_2\}\text{Al}^i\text{Bu}_2$ was isolated from the solution by crystallization at -30°C . Yield 1.84 g (2 crops), 69%. $^1\text{H NMR}$ (C_6D_6): δ 7.11 (m, 6H, NAr), 4.90 (s, 1H, CH), 3.46 (sept, $^3\text{J}_{\text{HH}} = 6.8$, 4H, CHMe_2), 1.90 (m, $^3\text{J}_{\text{HH}} = 6.5$, 2H, CH_2CHMe_2), 1.50 (s, 6H, CMe), 1.37 (d, $^3\text{J}_{\text{HH}} = 6.5$, 12H, CHMe_2), 1.15 (d, $^3\text{J}_{\text{HH}} = 6.5$, 12H, CHMe_2), 1.01 (d, $^3\text{J}_{\text{HH}} = 6.1$, 12H, CHMe_2), 0.14 (d, $^3\text{J}_{\text{HH}} = 6.8$, 4H, AlCH_2). $^{13}\text{C NMR}$ (C_6D_6): δ 170.1 (s, CMe), 144.3 (s, Ar-C_{ortho}), 141.8 (s, Ar-C_{ipso}), 127.1 (d, $^1\text{J}_{\text{CH}} = 161$, Ar-C_{para}), 124.5 (d, $^1\text{J}_{\text{CH}} = 157$, Ar-C_{meta}), 99.1 (d, $^1\text{J}_{\text{CH}} = 159$, CH), 28.8 (q, $^1\text{J}_{\text{CH}} = 124$, CHMe_2), 28.0 (d, $^1\text{J}_{\text{CH}} = 127$, CHMe_2), 27.1 (d, $^1\text{J}_{\text{CH}} = 123$, CHMe_2), 25.5 (q, $^1\text{J}_{\text{CH}} = 126$, CHMe_2), 24.9 (q, $^1\text{J}_{\text{CH}} = 126$, CHMe_2), 23.8 (q, $^1\text{J}_{\text{CH}} = 122$, CMe), 22.8 (br t, $^1\text{J}_{\text{CH}} = 109$, AlCH_2).

EXAMPLE 29

$\{\text{HC}(\text{CMeNAr}')_2\}\text{AlMe}_2$ ($\text{Ar}' = 2\text{-}^t\text{BuC}_6\text{H}_4$). This compound was prepared by the procedure described for $\{\text{HC}(\text{CMeNAr})_2\}\text{AlMe}_2$ ($\text{Ar} = 2,6\text{-}^i\text{PrC}_6\text{H}_3$), using 0.501 g $\text{HC}(\text{CMeNAr}')_2\text{H}$ (1.43 mmol) in 50 mL hexanes, and 0.103 g AlMe_3 (1.43 mmol) in 10 mL hexanes. A gas was evolved and the yellow solution became colorless after 1 h at room temperature. After a further 15 h the volatiles were removed to afford a yellow solid. Recrystallization from a concentrated Et_2O solution at -70°C afforded pure $\{\text{HC}(\text{CMeNAr}')_2\}\text{AlMe}_2$ (0.274 g, 46%). $^1\text{H NMR}$ (CD_2Cl_2): δ 7.53 (d, $^3\text{J}_{\text{HH}} = 6.8$, 1H, Ar'), 7.53 (d, $^3\text{J}_{\text{HH}} = 7.9$, 1H, Ar'), 7.22 (t, $^3\text{J}_{\text{HH}} = 7.2$, 1H, Ar'), 7.21 (t, $^3\text{J}_{\text{HH}} = 7.4$, 1H, Ar'), 7.18 (t, $^3\text{J}_{\text{HH}} = 7.0$, 1H, Ar'), 7.17 (t, $^3\text{J}_{\text{HH}} = 7.0$, 1H, Ar'), 6.92 (d, $^3\text{J}_{\text{HH}} = 7.2$, 1H, Ar'), 6.91 (d, $^3\text{J}_{\text{HH}} =$

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6.8, 1H, Ar'), 5.06 (s, 1H, CH), 1.75 (s, 6H, CMe), 1.42 (s, 18H, CMe₃), -0.72 (s, 3H, AlMe), -1.12 (s, 3H, AlMe). **¹³C NMR** (CD₂Cl₂): δ 170.8 (s, CMe), 144.4 (s, Ar'-C_{ipso} or C_{ortho}), 144.0 (s, Ar'-C_{ipso} or C_{ortho}), 130.1 (d, ¹J_{CH} = 153, Ar'), 129.4 (d, ¹J_{CH} = 158, Ar'), 126.9 (d, ¹J_{CH} = 160, Ar'), 126.5 (d, ¹J_{CH} = 159, Ar'), 97.1 (d, ¹J_{CH} = 160, CH), 36.7 (s, CMe₃), 32.9 (q, ¹J_{CH} = 126, CMe₃), 24.3 (q, ¹J_{CH} = 128, CMe), -8.36 (br q, ¹J_{CH} = 113, AlMe), -9.6 (br q, ¹J_{CH} = 113, AlMe). **Anal.** Calcd for C₂₇H₃₉AlN₂: C, 77.47; H, 9.39; N, 6.69. Found: C, 77.10; H, 9.17; N, 6.61. The structure of this compound was confirmed by X-ray crystallography.

EXAMPLE 30

[{HC(CMeNAr)₂}AlⁱBu][B(C₆F₅)₄]. This compound was prepared by the procedure described for Example 26, using 0.103 g {HC(CMeNAr)₂}AlⁱBu₂ (0.18 mmol) and 0.171 g [Ph₃C][B(C₆F₅)₄] (0.19 mmol). The presence of [{HC(CMeNAr)₂}AlⁱBu][B(C₆F₅)₄] and Ph₃CH was confirmed by NMR spectroscopy. **¹H NMR** (C₆D₆): δ 6.95 (m, 4H, NAr),* 5.34 (s, 1H, CH), 2.44 (br sept, ³J_{HH} = 6.8, 4H, CHMe₂), 1.51 (s, 6H, CMe), 1.12 (m, 1H, CH₂CHMe₂), 0.98 (d, ³J_{HH} = 6.1, 24H, CHMe₂), 0.22 (d, ³J_{HH} = 6.5, 6H, CH₂CHMe₂), 0.11 (d, ³J_{HH} = 6.5, 2H, CH₂CHMe₂). **¹³C NMR** (C₆D₆): δ 176.9 (s, CMe), 142.7 (s, Ar-C_{ortho}), 134.8 (s, Ar-C_{ipso}), 130.3 (d, ¹J_{CH} = 160, Ar-C_{para}), 125.6 (d, ¹J_{CH} = 161, Ar-C_{meta}), 104.0 (d, ¹J_{CH} = 168, CH), 29.8 (d, ¹J_{CH} = 127, CHMe₂), 26.6 (q, ¹J_{CH} = 125, CHMe₂), 24.2 (d, t, CHMe₂), 24.0 (q, ¹J_{CH} = 127, CHMe₂), 23.1 (q, ¹J_{CH} = 127, CHMe₂), 23.0 (q, ¹J_{CH} = 130, CMe), 17.2 (br t, ¹J_{CH} = 116, AlCH₂). * Remaining aromatic resonances

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obsured by overlap with Ph_3CH signals. † Splitting obscured by overlap.

EXAMPLE 31

5 $[\{\text{HC}(\text{CMeNAr})_2\}\text{AlMe}(\text{NMe}_2\text{Ph})][\text{B}(\text{C}_6\text{F}_5)_4]$. A CD_2Cl_2 solution (0.30 mL) of $[\text{HNMe}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]$ (0.054 g, 0.067 mmol) was added to a vial containing a solution of $\{\text{HC}(\text{CMeNAr})_2\}\text{AlMe}_2$ (0.032 g, 0.067 mmol) in CD_2Cl_2 (0.30 mL). A gas was evolved. The solution was transferred to an NMR tube and NMR spectra were recorded. ^1H NMR (CD_2Cl_2): δ 7.70 (m, 3H, $\text{NMe}_2\text{Ph} + \text{NAr}$), 7.54 (m, 2H, $\text{NMe}_2\text{Ph} + \text{NAr}$), 7.28 (m, 4H, $\text{NMe}_2\text{Ph} + \text{NAr}$), 7.21 (m, 2H, $\text{NMe}_2\text{Ph} + \text{NAr}$), 5.42 (s, 1H, CH), 3.64 (s, 6H, NMe_2Ph), 3.45 (sept, $^1J_{\text{HH}} = 6.7$, 2H, CHMe_2), 3.11 (sept, $^1J_{\text{HH}} = 6.8$, 2H, CHMe_2), 1.86 (s, 6H, CMe), 1.30 (d, $^1J_{\text{HH}} = 6.8$, 6H, CHMe_2), 1.25 (d, $^1J_{\text{HH}} = 7.2$, 6H, CHMe_2), 1.22 (d, $^1J_{\text{HH}} = 6.5$, 6H, CHMe_2), 1.10 (d, $^1J_{\text{HH}} = 6.8$, 6H, CHMe_2), -1.01 (s, 3H, AlMe).

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EXAMPLES 32-38**New Aluminum Guanidinate Complexes**EXAMPLE 32

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$\{\text{Me}_2\text{NC}(\text{N}^i\text{Pr})_2\}\text{AlCl}_2$. A slurry of LiNMe_2 (0.765 g, 15.0 mmol) in Et_2O (25 mL) was cooled to 0 °C, and a solution of 1,3-diisopropylcarbodiimide (1.89 g, 15.0 mmol) in Et_2O (15 mL) was added dropwise. The resulting mixture was allowed to warm to room temperature and stirred for 1 h. The mixture was cooled to -78 °C and a solution of AlCl_3 (2.00 g, 15.0 mmol) in Et_2O (15 mL) was added dropwise. The resulting mixture was allowed to warm to room temperature and stirred for 18 h. The volatiles were removed under vacuum and the product was extracted from the LiCl with toluene. The toluene extract was concentrated and cooled to

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-30 °C to yield clear, colorless crystals, which were isolated by filtration (2.20 g, 55% based on AlCl_3). ^1H NMR (CD_2Cl_2) δ 3.56 (sept, $^3J_{\text{HH}} = 6.3$, 2H, CHMe_2 , 2.96 (s, 6H, NMe_2), 1.12 (d, $^3J_{\text{HH}} = 6.1$, 12H, CHMe_2). ^{13}C NMR (CD_2Cl_2) δ 169.1 (s, CN_3), 45.7 (d, $^1J_{\text{CH}} = 138$, CHMe_2), 39.5 (q, $^1J_{\text{CH}} = 140$, NMe_2), 23.9 (q, $^1J_{\text{CH}} = 125$, CHMe_2). **Anal.** Calcd for $\text{C}_9\text{H}_{20}\text{AlCl}_2\text{N}_3$: C, 40.31; H, 7.52; N, 15.67. Found: C, 40.36; H, 7.74; N, 15.39. The structure of this compound was confirmed by X-ray crystallography.

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EXAMPLE 33

$\{\text{Et}_2\text{NC}(\text{N}^i\text{Pr})_2\}\text{AlCl}_2$. This compound was prepared by the procedure outlined for $\{\text{Me}_2\text{NC}(\text{N}^i\text{Pr})_2\}\text{AlCl}_2$, using 1.19 g of LiNEt_2 (15.0 mmol) 1.89 g of 1,3-diisopropylcarbodiimide (15.0 mmol), and 2.00 g of AlCl_3 (15.0 mmol). This complex was crystallized from toluene at -30°C and isolated as clear, colorless crystals (3.01 g, 68% based on AlCl_3). ^1H NMR (CD_2Cl_2) δ 3.46 (sept, $^3J_{\text{HH}} = 6.4$, 2H, CHMe_2), 3.33 (q, $^3J_{\text{HH}} = 7.1$, 4H, $\text{N}(\text{CH}_2\text{CH}_3)_2$), 1.19 (t, $^3J_{\text{HH}} = 6.7$, 6H, $\text{N}(\text{CH}_2\text{CH}_3)_2$), 1.14 (d, $^3J_{\text{HH}} = 6.1$, 12H, CHMe_2). ^{13}C NMR (CD_2Cl_2): δ 168.8 (s, CN_3), 45.8 (d, $^1J_{\text{CH}} = 137$, CHMe), 43.1 (t, $^1J_{\text{CH}} = 136$, CH_2Me), 24.1 (q, $^1J_{\text{CH}} = 127$, CHMe), 12.9 (q, $^1J_{\text{CH}} = 127$, CH_2Me). **Anal.** Calcd for $\text{C}_{11}\text{H}_{24}\text{AlCl}_2\text{N}_3$: C, 44.60; H, 8.17; N, 14.19. Found: C, 44.58; H, 7.89; N, 14.04. **MS** (EI, m/z , ^{35}Cl): 295 $[\text{M}]^+$, 280 $[\text{M}-\text{Me}]^+$.

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EXAMPLE 34

$\{^i\text{Pr}_2\text{NC}(\text{N}^i\text{Pr})_2\}\text{AlCl}_2$. This compound was prepared by

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the procedure outlined for $\{\text{Me}_2\text{NC}(\text{N}^i\text{Pr})_2\}\text{AlCl}_2$, using 1.61 g of LiN^iPr_2 (15.0 mmol), 1.89 g of 1,3-diisopropylcarbodiimide (15.0 mmol), and 2.00 g of AlCl_3 (15.0 mmol). This complex was isolated as pale yellow crystals (1.134 g, 40.8% based on AlCl_3). ^1H NMR (CD_2Cl_2) δ 3.77 (sept, $^3J_{\text{HH}} = 6.8$, $\text{N}(\text{CHMe}_2)_2$), 3.55 (sept, $^3J_{\text{HH}} = 6.2$, NCHMe_2), 1.37 (d, $^3J_{\text{HH}} = 6.8$, $\text{N}(\text{CHMe}_2)_2$), 1.18 (d, $^3J_{\text{HH}} = 5.8$, NCHMe_2). ^{13}C NMR (CD_2Cl_2): δ 172.5 (s, CN_3), 51.1 (d, $^1J_{\text{CH}} = 136$, CHMe_2), 45.9 (d, $^1J_{\text{CH}} = 135$, CHMe_2), 24.7 (q, $^1J_{\text{CH}} = 125$, CHMe_2), 23.5 (q, $^1J_{\text{CH}} = 125$, CHMe_2). **Anal.** Calcd for $\text{C}_{13}\text{H}_{28}\text{AlCl}_2\text{N}_3$: C, 48.15; H, 8.70; N, 12.96. Found: C, 47.87; H, 8.68; N, 12.96. MS (EI, m/z , ^{35}Cl): 295 $[\text{M}]^+$, 280 $[\text{M} - \text{Me}]^+$.

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EXAMPLE 35

$\{(\text{Me}_3\text{Si})_2\text{NC}(\text{N}^i\text{Pr})_2\}\text{AlCl}_2$. This compound was prepared by the procedure outlined for $\{\text{Me}_2\text{NC}(\text{N}^i\text{Pr})_2\}\text{AlCl}_2$, using 2.00 g of $\text{LiN}(\text{SiMe}_3)_2$ (12.0 mmol), 1.51 g of 1,3-diisopropylcarbodiimide (12.0 mmol), and 1.59 g of AlCl_3 (12.0 mmol). The complex was extracted from the LiCl , recrystallized from pentane and isolated as white crystals (1.41 g, 40.8% based on AlCl_3). ^1H NMR (CD_2Cl_2) δ 3.60 (sept, $^3J_{\text{HH}} = 6.6$, 2H, CHMe_2), 1.14 (d, $^3J_{\text{HH}} = 6.5$, 12H, CHMe_2), 0.30 (s, 18H, SiMe_3). ^{13}C NMR (CD_2Cl_2) δ 172.4 (s, CN_3), 44.5 (d, $^1J_{\text{CH}} = 134$, CHMe_2), 25.3 (q, $^1J_{\text{CH}} = 124$, CHMe_2), 2.0 (q, $^1J_{\text{CH}} = 119$, SiMe_3). **Anal.** Calcd for $\text{C}_{13}\text{H}_{32}\text{AlCl}_2\text{N}_3\text{Si}_2$: C, 40.61; H, 8.39; N, 10.63. Found: C, 40.44; H, 8.24; N, 10.72. MS (EI, m/z , ^{35}Cl): 368 $[\text{M} - \text{Me}]^+$.
The structure of this compound was confirmed by X-ray crystallography.

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EXAMPLE 36

{Me₂NC(NⁱPr)₂}AlMe₂. This compound was prepared by the procedure outlined for {Me₂NC(NⁱPr)₂}AlCl₂, using 0.809 g of
5 LiNMe₂ (15.9 mmol), 2.00 g of 1,3-diisopropylcarbodiimide (15.9 mmol), and 1.47 mL of AlMe₂Cl (15.9 mmol). The complex was extracted from the LiCl with pentane. The volatiles were removed under vacuum to afford a sticky yellow solid. Clear, colorless crystals were obtained by
10 sublimation at 60°C onto a dry ice probe (0.30 g, 64.7% based on AlMe₂Cl). Note, because the complex is a liquid at room temperature a small aluminum pan was positioned beneath the cold probe of the sublimator to collect the sublimed product as it melted. ¹H NMR (CD₂Cl₂): δ 3.50 (sept, ³J_{HH}
15 = 6.3, 2H, CHMe₂), 2.85 (s, 6H, NMe₂), 1.02 (d, ³J_{HH} = 6.1, 12H, CHMe₂), -0.82 (s, 6H, AlMe₂). ¹³C NMR (CD₂Cl₂) δ 167.6 (s, CN₃), 45.2 (d, ¹J_{CH} = 135, CHMe₂), 39.2 (q, ¹J_{CH} = 136, NMe₂), 24.3 (q, ¹J_{CH} = 125, CHMe₂), -8.7 (q, ¹J_{CH} = 110, AlMe₂). **Anal.** Calcd for C₁₁H₂₆AlN₃: C, 58.12; H, 11.53; N,
20 18.48. Found: C, 57.97; H, 11.70; N, 18.25. MS (EI, m/z): 212 [M - Me]⁺.

EXAMPLE 37

25 **{Et₂NC(NⁱPr)₂}AlMe₂.** This compound was prepared by the procedure outlined for {Me₂NC(NⁱPr)₂}AlCl₂, using 1.25 g of LiNEt₂ (15.9 mmol), 2.00 g of 1,3-diisopropylcarbodiimide (15.9 mmol), and 1.47 mL of AlMe₂Cl (15.9 mmol). The product was extracted from the LiCl with pentane and the
30 volatiles were removed under vacuum to afford a sticky orange solid, from which white crystals (2.39 g, 59% based on AlMe₂Cl) were isolated by sublimation at 60°C onto a dry ice cooled probe. ¹H NMR (CD₂Cl₂): δ 3.41 (sept, ³J_{HH} =

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6.3, 2H, CHMe₂), 3.21 (q, ³J_{HH} = 7.3, 4H, N(CH₂CH₃)₂), 1.14 (t, ³J_{HH} = 7.2, 6H, N(CH₂CH₃)₂), 1.03, (d, ³J_{HH} = 6.5, 12H, CHMe₂), -0.82 (s, 6H, AlMe₂). ¹³C NMR (CD₂Cl₂) δ 167.3 (s, CN₃), 45.3 (d, ¹J_{CH} = 135, CHMe₂), 42.6 (t, ¹J_{CH} = 136, N(CH₂CH₃)₂), 24.6 (q, ¹J_{CH} = 126, CHMe₂), 13.2 (q, ¹J_{CH} = 126, N(CH₂CH₃)₂), -8.6 (q, ¹J_{CH} = 112, AlMe₂). **Anal.** Calcd for C₁₃H₃₀AlN₃: C, 61.14; H, 11.84; N, 16.45. Found: C, 60.88; H, 11.97; N, 16.30. MS (EI, m/z): 240 [M - Me]⁺.

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EXAMPLE 38

{ⁱPr₂NC(NⁱPr)₂}AlMe₂. This compound was prepared by the procedure outlined for {Me₂NC(NⁱPr)₂}AlCl₂, using 4.24 g of LiNⁱPr₂ (39.6 mmol), 5.00 g of 1,3-diisopropylcarbodiimide (39.6 mmol), and 3.68 mL of AlMe₂Cl (39.6 mmol). The product was extracted from the LiCl with pentane and the volatiles were removed under vacuum to afford a reddish-brown liquid from which white crystals were obtained by recrystallization from pentane in a -78°C cold bath (5.26 g, 46.8% yield based on AlMe₂Cl). Analytically pure, waxy, white crystals were obtained by vacuum sublimation at 65°C onto a dry ice probe (2.54 g, 22.6% yield based on AlMe₂Cl). The low final yield is due to the compound's high solubility in pentane. ¹H NMR (CD₂Cl₂): δ 3.59 (sept, ³J_{HH} = 5.7, 2H, N(CHMe₂)₂), 3.52 (sept, ³J_{HH} = 6.0, 2H, NCHMe₂), 1.22 (d, ³J_{HH} = 7.2, 12H, N(CHMe₂)₂), 1.04 (d, ³J_{HH} = 6.1, 12H, NCHMe₂), -0.81 (s, 6H, AlMe₂). ¹³C NMR (CD₂Cl₂) δ 168.1 (s, CN₃), 49.1 (d, ¹J_{CH} = 132, N(CHMe₂)₂), 45.0 (d, ¹J_{CH} = 133, NCHMe₂), 25.5 (q, ¹J_{CH} = 125, N(CHMe₂)₂), 23.3 (q, ¹J_{CH} = 126, NCHMe₂), -9.4 (q, ¹J_{CH} = 115, AlMe₂).

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EXAMPLE 39**Ethylene Polymerization Using an Aluminum Guanidinate Catalyst**

5 A solution of $\{^i\text{Pr}_2\text{NC}(^i\text{Pr})_2\}\text{AlMe}_2$ (120 mg, 0.423 mmol) in toluene was slowly added to a stirred solution of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (390 mg, 0.423 mmol) in toluene. A red oil layer immediately appeared at the bottom of the flask. The reaction mixture was stirred for 1 h and then was exposed to
10 ethylene (1 atm). A white solid appeared immediately. The mixture was stirred 18 h and then was quenched with acidified methanol (50 mL). the polymer was collected by filtration, washed with 80 mL acidified water, and dried to yield 340 mg of polyethylene.

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EXAMPLES 40-48**Gallium Amidinate Complexes**

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EXAMPLE 40

$\{^t\text{BuC}(^i\text{Pr})_2\}\text{GaCl}_2$. A colorless solution of GaCl_3 (0.840 g, 4.75 mmol) in Et_2O (10 mL) was cooled to -78°C and added dropwise to a slurry of $\text{Li}[\{^t\text{BuC}(^i\text{Pr})_2\}]$ (0.904 g, 4.75 mmol)
25 in Et_2O (40 mL), also at -78°C . The mixture was allowed to warm to room temperature and was stirred for 12 h affording a slurry of a white solid in a pale yellow solution. The mixture was filtered and the filtrate was concentrated to 30 mL and cooled at -78°C to yield pure $\{^t\text{BuC}(^i\text{Pr})_2\}\text{GaCl}_2$ as
30 colorless crystals that were collected by filtration (0.970 g, 64%). $^1\text{H NMR}$ (C_6D_6): δ 3.82 (septet, $^3J = 6.5$, 2H, CHMe_2), 1.14 (d, $^3J = 6.2$, 12H, CHMe_2), 0.96 (s, 9H, CMe_3). $^{13}\text{C NMR}$ (C_6D_6): δ 179.6, 47.5, 38.5, 28.6, 25.7. **Anal.** Calcd for $\text{C}_{11}\text{H}_{23}\text{Cl}_2\text{GaN}_2$: C, 40.78; H, 7.17; N, 8.65. Found: C, 40.45;
35 H, 6.92; N, 8.57. **EI-MS.** (m/z): 324 $[\text{M}]^+$, 309 $[\text{M}-\text{CH}_3]^+$.

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EXAMPLE 41

{^tBuC(NCy)₂}GaCl₂. The procedure described above for {^tBuC(NⁱPr)₂}GaCl₂ was followed using GaCl₃ (0.840 g, 4.75 mmol) and Li[^tBuC(NCy)₂] (1.28 g, 4.75 mmol). Recrystallization from Et₂O yielded to pure {^tBuC(NCy)₂}GaCl₂ as colorless crystals that were collected by filtration (1.21 g, 63%). ¹H NMR (C₆D₆): δ 3.58 (br m, 2H, Cy), 1.96 (br d, 4H, Cy), 1.64-1.42 (br m, 10H, Cy), 1.07 (s, 9H, CMe₃), 1.3-0.9 (br m, 6H, Cy). ¹³C NMR (C₆D₆): δ 179.8 (s, CCMe₃), 55.7 (d, ¹J_{CH} = 138, Cy-C₁), 38.6 (s, CMe₃), 36.9 (t, ¹J_{CH} = 128, Cy), 28.7 (q, ¹J_{CH} = 127, CMe₃), 25.4 (t, ¹J_{CH} = 127, Cy), 25.2 (t, ¹J_{CH} = 126, Cy). **Anal.** Calcd for C₁₇H₃₁Cl₂GaN₂: C, 50.52; H, 7.75; N, 6.93. Found: C, 50.41; H, 7.85; N, 6.93.

EI-MS. (m/z): 404 [M]⁺.

EXAMPLE 42

{^tBuC(NⁱPr)₂}GaMe₂. {^tBuC(NⁱPr)₂}GaCl₂ was generated *in situ* in Et₂O (50 mL) as described above. The resulting mixture was cooled to -78 °C and 2 equiv of CH₃MgCl (6.34 mL of a 3.0 M solution in THF, 19.1 mmol) was added dropwise by syringe. The reaction mixture was allowed to warm to room temperature and was stirred for 15 h. The volatiles were removed under reduced pressure affording a pale yellow solid that was extracted with hexanes (70 mL). The extract was concentrated to 15 mL and cooled to -78 °C to yield pure {^tBuC(NⁱPr)₂}GaMe₂ as colorless crystals which were collected by filtration (1.36 g, 51%). ¹H NMR (C₆D₆): δ 4.10 (septet, ³J = 6.1, 2H, CHMe₂), 1.21 (s, 9H, CMe₃), 1.12 (d, ³J = 6.1, 12H, CHMe₂), 0.24 (s, 6H, GaMe₂). ¹³C NMR (C₆D₆): δ 173.9 (s, CCMe₃), 46.3 (d, ¹J_{CH} = 139, CHMe₂), 39.3 (s, CMe₃), 29.6 (q,

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$^1J_{CH} = 127$, $CHMe_2$), 26.2 (q, $^1J_{CH} = 125$, CMe_3), -4.74 (q, $^1J_{CH} = 123$, $GaMe_2$). **Anal.** Calcd for $C_{13}H_{29}GaN_2$: C, 55.14; H, 10.34; N, 9.89. Found: C, 55.18; H, 10.44; N, 9.90. **EI-MS.** (m/z): 267 $[M-CH_3]^+$.

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EXAMPLE 43

$\{^tBuC(NCy)_2\}GaMe_2$. $\{^tBuC(NCy)_2\}GaCl_2$ was generated *in situ* in Et_2O (50 mL) as described above. The resulting mixture was cooled to $-78^\circ C$ and CH_3MgCl (6.34 mL of a 3.0 M solution in THF, 19.1 mmol) was added dropwise by syringe. The reaction mixture was allowed to warm to room temperature and was stirred for 15 h. The volatiles were removed under reduced pressure affording a pale yellow solid that was extracted with hexanes (70 mL). The extract was concentrated to 15 mL and cooled to $-78^\circ C$ to yield pure $\{^tBuC(NCy)_2\}GaMe_2$ as large colorless crystals which were collected by filtration (1.81 g, 53%). **1H NMR** (C_6D_6): δ 3.72 (br m, 2H, Cy), 2.00-1.95 (br d, 4H, Cy), 1.74-1.70 (br d, 4H, Cy), 1.61-1.57 (br d, 2H, Cy), 1.30-1.00 (br m, 10H, Cy), 1.29 (s, 9H, CMe_3), 0.26 (s, 6H, $GaMe_2$). **^{13}C NMR** (C_6D_6): δ 174.1 (s, $CCMe_3$), 55.0 (d, $^1J_{CH} = 128$, Cy- C_1), 39.4 (s, CMe_3), 37.5 (t, $^1J_{CH} = 127$, Cy), 29.7 (q, $^1J_{CH} = 122$, CMe_3), 26.0 (t, $^1J_{CH} = 125$, Cy), 25.9 (t, $^1J_{CH} = 125$, Cy), -4.64 (q, $^1J_{CH} = 120$, $GaMe_2$). **Anal.** Calcd for $C_{19}H_{37}GaN_2$: C, 62.81; H, 10.28, N 7.71. Found: C, H, N. **EI-MS.** (m/z): 348 $[M]^+$.

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EXAMPLE 44

$\{^tBuC(N^iPr)_2\}Ga(CH_2Ph)_2$. $\{^tBuC(N^iPr)_2\}GaCl_2$ was generated *in situ* in Et_2O (50 mL) as described above. The resulting mixture was cooled to $-78^\circ C$ and $PhCH_2MgCl$ (9.51 mL of a 1.0 M solution in Et_2O , 9.51 mmol) was added dropwise by

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syringe. The reaction mixture was allowed to warm to room temperature and was stirred for 15 h. The volatiles were removed under reduced pressure affording a pale yellow oil that was extracted with hexanes (70 mL). The extract was
5 dried under vacuum for 12 h yielding pure $\{^t\text{BuC}(\text{N}^i\text{Pr})_2\}\text{Ga}(\text{CH}_2\text{Ph})_2$ as a colorless oil (1.36 g, 51%). **^1H NMR** (C_6D_6): δ 7.30-7.24 (m, 8H, o-and m-Ph), 7.1-7.0 (m, 2H, p-Ph), 3.90 (septet, $^3J = 5.8$, 2H, CHMe_2), 2.35 (s, 4H, CH_2Ph), 1.14 (s, 9H, CMe_3), 0.88 (d, $^3J = 6.1$, 12H, CHMe_2).
10 **^{13}C NMR** (C_6D_6): δ 175.9 (s, CCMe_3), 145.4 (s, ipso-Ph), 128.4 (d, $^1J_{\text{CH}} = 160$, o-or m-Ph), 127.9 (d, $^1J_{\text{CH}} = 155$, o- or m-Ph), 122.6 (d, $^1J_{\text{CH}} = 165$, p-Ph), 45.9 (d, $^1J_{\text{CH}} = 136$, CHMe_2), 39.2 (s, CMe_3), 29.5 (q, $^1J_{\text{CH}} = 127$, CHMe_2), 26.2 (q, $^1J_{\text{CH}} = 129$, CMe_3), 23.6 (t, $^1J_{\text{CH}} = 123$, CH_2Ph). **Anal.** Calcd for
15 $\text{C}_{25}\text{H}_{37}\text{GaN}_2$: C, 68.97; H, 8.58; N 6.44. Found: C, 69.00; H, 8.68; N, 6.44. **EI-MS.** (EI, m/z): 434 $[\text{M}]^+$, 343 $[\text{M}-\text{C}_7\text{H}_9]^+$.

EXAMPLE 45

20 $\{^t\text{BuC}(\text{N}^t\text{Bu})_2\}\text{GaCl}_2$. A colorless solution of di- ^tBu -carbodiimide (2.0 g, 13.0 mmol) in Et_2O (35 mL) was cooled to 0 °C and $^t\text{BuLi}$ (7.62 mL of a 1.7 M solution in pentane, 13.0 mmol) was added dropwise by syringe. The reaction mixture was allowed to warm to room temperature and was stirred for 1
25 h resulting in a white slurry. A colorless solution of GaCl_3 (2.3 g, 13.0 mmol) in Et_2O (10 mL) cooled at -78 °C was added dropwise to the mixture also cooled at -78 °C. The resulting mixture was allowed to warm to room temperature and was stirred for 12 h affording a slurry of a white solid in a
30 pale yellow solution. The mixture was filtered and the filtrate was concentrated to 25 mL and cooled at -78 °C to yield pure $\{^t\text{BuC}(\text{N}^t\text{Bu})_2\}\text{GaCl}_2$ as colorless crystals that were

collected by filtration (0.71 g, 17%). ^1H NMR (C_6D_6): δ 1.41 (s, 18H, N CMe_3), 1.13 (s, 9H, CCMe_3). ^{13}C NMR (C_6D_6): δ 183.7 (CCMe_3), 56.0 (NCMe_3), 37.3 (CCMe_3), 34.0 (NCMe_3), 31.2 (CCMe_3). **Anal.** Calcd for $\text{C}_{13}\text{H}_{27}\text{Cl}_2\text{GaN}_2$: C, 44.36; H, 7.75; N, 7.96. Found: C, 44.43; H, 7.82; N, 7.70. The structure of this compound was confirmed by X-ray crystallography.

EXAMPLE 46

10 $\{\text{tBuC}(\text{NCy})_2\}\text{Ga}(\text{CH}_2\text{Ph})_2$. A colorless solution of $\{\text{tBuC}(\text{NCy})_2\}\text{GaCl}_2$ (1.03 g, 2.55 mmol) in Et_2O (40 mL) was cooled to -78°C and PhCH_2MgCl (5.10 mL of a 1.0 M solution in Et_2O , 5.10 mmol) was added dropwise by syringe. The reaction mixture was allowed to warm to room temperature and was stirred for 15 h. The volatiles were removed under reduced pressure affording a pale yellow oil that was extracted with hexanes (70 mL). The extract was dried under vacuum for 12 h yielding pure $\{\text{tBuC}(\text{NCy})_2\}\text{Ga}(\text{CH}_2\text{Ph})_2$ as a colorless oil (1.31 g, 70%). ^1H NMR (C_6D_6): δ 7.33-7.26 (m, 8H, o- and m-Ph), 7.10-7.05 (m, 2H, p-Ph), 3.54 (m, 2H, Cy), 2.40 (s, 4H, CH_2Ph), 1.73-1.56 (m, 10H, Cy), 1.21 (s, CMe_3), 1.17-0.80 (m, 10H, Cy). ^{13}C NMR (C_6D_6): δ 175.9 (s, CCMe_3), 145.6 (s, ipso-Ph), 128.4 (d, $^1J_{\text{CH}} = 158$, o- or m-Ph), 128.0 (d, $^1J_{\text{CH}} = 156$, o- or m-Ph), 122.7 (d, $^1J_{\text{CH}} = 155$, p-Ph), 54.6 (d, $^1J_{\text{CH}} = 132$, C1-Cy), 39.2 (s, CMe_3), 37.2 (t, $^1J_{\text{CH}} = 127$, Cy), 29.6 (q, $^1J_{\text{CH}} = 131$, CMe_3), 25.8 (t, $^1J_{\text{CH}} = 125$, Cy), 25.7 (t, $^1J_{\text{CH}} = 125$, Cy), 23.8 (t, $^1J_{\text{CH}} = 124$, CH_2Ph).

EXAMPLE 47

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$\{\text{tBuC}(\text{N}^i\text{Pr})_2\}\text{GaEt}_2$. $\{\text{tBuC}(\text{N}^i\text{Pr})_2\}\text{GaCl}_2$ (1a) was generated in situ in Et_2O (50 mL) as described above. The resulting mixture was cooled to -78°C and of EtMgCl (9.51 mL

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of a 2.0 M solution in Et₂O, 19.1 mmol, 2 equiv) was added dropwise by syringe. The reaction mixture was allowed to warm to room temperature and was stirred for 15 h. The volatiles were removed under reduced pressure affording a pale yellow solid that was extracted with hexanes (70 mL). The extract was dried under vacuum for 12 h yielding pure {^tBuC(NⁱPr)₂}GaEt₂ as a colorless oil (1.72 g, 58%). ¹H NMR (C₆D₆): δ 4.06 (septet, ³J = 6.1, 2H, CHMe₂), 1.55 (t, ³J = 7.9, 6H, GaCH₂CH₃), 1.23 (s, CMe₃, 9H), 1.12 (d, ³J = 6.5, CHMe₂, 12H), 0.85 (q, ³J = 7.9, 4H, GaCH₂CH₃). ¹³C NMR (C₆D₆): δ 173.9 (s, CCMe₃), 46.3 (d, ¹J_{CH} = 139, CHMe₂), 39.3 (s, CMe₃), 29.6 (q, ¹J_{CH} = 127, CHMe₂), 26.2 (q, ¹J_{CH} = 125, CMe₃), -4.74 (q, ¹J_{CH} = 123, GaMe₂).

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EXAMPLE 48

[{^tBuC(NⁱPr)₂}Ga(CH₂Ph)][B(C₆F₅)₄]. C₆D₆ (0.5 mL) was vacuum transferred at -78 °C to a mixture of {^tBuC(NⁱPr)₂}Ga(CH₂Ph)₂ (84.0 mg, 0.193 mmol) and [Ph₃C][B(C₆F₅)₄] (178 mg, 0.193 mmol) in a resealable NMR tube. The tube was warmed to 23 °C and vigorously shaken. The reaction mixture separated into two phases: a dark orange phase at the bottom of the tube and a light yellow phase on the top. After 15 min at 23 °C, the bottom layer was analyzed by ¹H NMR which indicated that [{^tBuC(NⁱPr)₂}Ga(CH₂Ph)][B(C₆F₅)₄] was the major species (70% NMR yield). ¹H NMR (C₆D₆): δ 3.75 (septet, ³J = 6.1 Hz, 2H, CHMe₂), 1.43 (s, 2H, GaCH₂Ph), 1.03 (s, 9H, CMe₃), 0.63 (d, ³J = 6.1 Hz, 12H, CHMe₂).

EXAMPLE 49-50**Ethylene Polymerizations By a Gallium Amidinate Catalyst**5 EXAMPLE 49

A solution of $\{^t\text{BuC}(\text{N}^i\text{Pr})_2\}\text{GaMe}_2$ (0.2 mmol) in toluene (20 mL) was prepared and 1 equiv. of $\text{B}(\text{C}_6\text{F}_5)_3$ was added. The
10 mixture was put in a preheated oil bath at 50 °C, charged with 4 atm of ethylene and vigorously stirred for 3 h. The mixture was allowed to cool to room temperature and quenched with 100 mL of methanol. The polymer was collected by filtration and dried under vacuum to afford 12 mg polyethylene.

15 EXAMPLE 50

A solution of $\{^t\text{BuC}(\text{N}^i\text{Pr})_2\}\text{Ga}(\text{CH}_2\text{Ph})_2$ (0.2 mmole) in toluene (20 mL) was prepared and 1 equiv. of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$
20 was added. The mixture was put in a preheated oil bath at 50 °C, charged with 4 atm of ethylene and vigorously stirred for 3 h. The mixture was allowed to cool to room temperature and quenched with 100 mL of methanol. The polymer was collected by filtration and dried under vacuum to afford 65 mg
25 polyethylene.

EXAMPLES 51-55**Aluminum Aminotroponimate Complexes**30 EXAMPLE 51

$\{(^i\text{Pr})_2\text{ATI}\}\text{Al}(\text{Et})_2$. A hexane solution (ca. 20 mL) of $\{(^i\text{Pr})_2\text{ATI}\}\text{H}$ (1.0 g, 4.9 mmol) was added to a solution of
35 AlEt_3 (0.6 g, 5 mmol) in hexane at 0 °C. The mixture was allowed to warm to 23 °C and stirred overnight. A small amount of insoluble solid was removed by filtration. The volatiles were removed under vacuum leaving a yellow solid. Recrystallization of this solid from pentane afforded

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{{ⁱPr)₂ATI}AlEt₂ as yellow powder (0.65 g, 46%). ¹H NMR (C₆D₆): δ 6.75 (dd, ³J_{HH} = 10.4, 10.4, 2H, H_{4,6}), 6.34 (d, ³J_{HH} = 11.5, 2H, H_{3,7}), 6.21 (t, ³J_{HH} = 9.4, 1H, H₅), 3.54 (sept, ³J_{HH} = 6.5, 2H, NCHMe₂), 1.34 (t, ³J_{HH} = 8.3, 6H, AlCH₂CH₃), 1.22 (d, ³J_{HH} = 6.8, 12H, NCHMe₂), 0.38 (q, ³J_{HH} = 7.9, 4H, AlCH₂CH₃). ¹³C NMR (C₆D₆): δ 161.6 (s, C_{2,8}), 136.5 (d, ¹J_{CH} = 153, C_{4,6}), 119.1 (d, ¹J_{CH} = 160, C_{3,7}), 113.7 (d, ¹J_{CH} = 151, C₅), 47.5 (d, ¹J_{CH} = 135, NCHMe₂), 22.2 (q, ¹J_{CH} = 125, NCHMe₂), 9.87 (q, ¹J_{CH} = 124, AlCH₂CH₃), 4.18 (t, ¹J_{CH} = 115, AlCH₂CH₃).

EXAMPLE 52

{{ⁱPr)₂ATI}Al(ⁱBu)₂. A hexane solution (ca. 20 mL) of {{ⁱPr)₂ATI}H (1.17 g, 5.73 mmol) was added to a solution of Al(ⁱBu)₃ (1.27 g, 6.40 mmol) in hexane at 0 °C. The mixture was allowed to warm to 23 °C and stirred overnight. A small amount of insoluble solid was removed by filtration. The volatiles were removed under vacuum leaving a yellow solid. Recrystallization of this solid from pentane afforded {{ⁱPr)₂ATI}Al(ⁱBu)₂ as yellow crystals (0.95 g, 48%). ¹H NMR (C₆D₆): δ 6.76 (dd, ³J_{HH} = 11.5, 9.0, 2H, H_{4,6}), 6.36 (d, ³J_{HH} = 11.9, 2H, H_{3,7}), 6.20 (t, ³J_{HH} = 9.0, 1H, H₅), 3.58 (sept, ³J_{HH} = 6.5, 2H, NCHMe₂), 2.01 (nonet, ³J_{HH} = 6.5, 2H, AlCH₂CHMe₂), 1.27 (d, ³J_{HH} = 6.8, 12H, NCHMe₂), 1.12 (d, ³J_{HH} = 6.1, 12H, AlCH₂CHMe₂), 0.38 (d, ³J_{HH} = 6.8, 4H, AlCH₂CHMe₂). ¹³C NMR (C₆D₆): δ 161.6 (s, C_{2,8}), 136.4 (d, ¹J_{CH} = 151, C_{4,6}), 119.2 (d, ¹J_{CH} = 158, C_{3,7}), 114.2 (d, ¹J_{CH} = 151, C₅), 47.5 (d, ¹J_{CH} = 135, NCHMe₂), 28.7 (q, ¹J_{CH} = 124, NCHMe₂), 27.3 (d, ¹J_{CH} = 124, AlCH₂CHMe₂), 26.5 (t, ¹J_{CH} = 107,

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AlCH₂CHMe₂), 22.3 (q, ¹J_{CH} = 126, AlCH₂CHMe₂). Anal. Calcd for C₂₁H₃₇N₂Al: C, 73.21; H, 10.82; N, 8.13. Found: C, 73.07; H, 11.04; N, 8.01.

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EXAMPLE 53

[{(ⁱPr)₂ATI}AlEt][B(C₆F₅)₄]. {(ⁱPr)₂ATI}AlEt₂ (0.104 g, 0.361 mmol) and [Ph₃C][B(C₆F₅)₄] (0.303 g, 0.328 mmol) were placed in a vial. Benzene (ca. 0.5 mL) was added and the mixture was stirred for 0.5 h. Hexane (ca. 5 mL) was added, the mixture was stirred and a yellow precipitate formed. The supernatant was removed using a pipette. The yellow solid was washed with hexane 4 times, collected by filtration and dried under vacuum affording [(ⁱPr)₂ATI}AlEt][B(C₆F₅)₄] as yellow powder (226 mg, 74 %). ¹H NMR (ClC₆D₅): δ 6.91 (dd, ³J_{HH} = 10.4, 10.4, 2H, H_{4,6}), 6.53 (t, ³J_{HH} = 9.7, 1H, H₅), 6.49 (d, ³J_{HH} = 11.2, 2H, H_{3,7}), 3.26 (sept, ³J_{HH} = 6.5, 2H, NCHMe₂), 0.84 (d, ³J_{HH} = 6.1, 12H, NCHMe₂), 0.79 (t, ³J_{HH} = 8.3, 3H, AlCH₂CH₃), 0.19 (q, ³J_{HH} = 6.5, 2H, AlCH₂CH₃). ¹³C NMR (C₆D₆, 50 °C): δ 159.6 (s, C_{2,8}), 149.1 (d, ¹J_{CF} = 240, B(C₆F₅)₄⁻), 138.9 (d, ¹J_{CH} = 156, C_{4,6}), 138.8 (d, ¹J_{CF} = 245, B(C₆F₅)₄⁻), 137.1 (d, ¹J_{CF} = 245, B(C₆F₅)₄⁻), 129.5 (d, ¹J_{CH} = 161, C_{3,7}), 125.2 (br, ipso-B(C₆F₅)₄⁻), 120.8 (d, ¹J_{CH} = 154, C₅), 47.2 (d, ¹J_{CH} = 138, NCHMe₂), 22.7 (q, ¹J_{CH} = 127, NCHMe₂), 7.06 (q, ¹J_{CH} = 128, AlCH₂CH₃), 3.24 (t, ¹J_{CH} = 120, AlCH₂CH₃). Anal. Calcd for C₃₉H₂₄AlBF₂₀N₂: C, 49.92; H, 2.58; N, 2.99. Found: C, 50.08; H, 2.73; N, 2.90.

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EXAMPLE 54

[{(ⁱPr)₂ATI}AlⁱBu][B(C₆F₅)₄]. {(ⁱPr)₂ATI}Al(ⁱBu)₂ (0.141 g, 0.409 mmol) and [Ph₃C][B(C₆F₅)₄] (0.350 g, 0.379

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mmol) were placed in a vial. Benzene (ca. 0.5 mL) was added and the mixture was stirred for 0.5 h. Hexane (ca. 5 mL) was added, the mixture was stirred and a yellow precipitate formed. The supernatant was removed by pipette. The yellow solid was washed with hexane 5 times, collected by filtration and dried under vacuum affording $[(i\text{Pr})_2\text{ATI})\text{Al}(i\text{Bu})_2][\text{B}(\text{C}_6\text{F}_5)_4]$ as a yellow powder (244 mg, 67 %). ^1H NMR (C_6D_6 , 60 °C): δ 7.23 (dd, $^3J_{\text{HH}} = 10.3, 10.1$, 2H, $\text{H}_{4,6}$), 6.98 (d, $^3J_{\text{HH}} = 11.2$, 2H, $\text{H}_{3,7}$), 6.86 (t, $^3J_{\text{HH}} = 9.4$, 1H, H_5), 3.59 (sept, $^3J_{\text{HH}} = 6.5$, 2H, NCHMe_2), 1.91 (nonet, $^3J_{\text{HH}} = 6.8$, 2H, $\text{AlCH}_2\text{CHMe}_2$), 1.06 (d, $^3J_{\text{HH}} = 6.1$, 12H, NCHMe_2), 0.93 (d, $^3J_{\text{HH}} = 6.5$, 6H, $\text{AlCH}_2\text{CHMe}_2$), 0.64 (d, $^3J_{\text{HH}} = 7.6$, 2H, $\text{AlCH}_2\text{CHMe}_2$). ^{13}C NMR (C_6D_6 , 50 °C): δ 159.6 (s, $\text{C}_{2,8}$), 149.1 (d, $^1J_{\text{CF}} = 242$, $\text{B}(\text{C}_6\text{F}_5)_4^-$), 139.1 (d, $^1J_{\text{CH}} = 157$, $\text{C}_{4,6}$), 138.8 (d, $^1J_{\text{CF}} = 246$, $\text{B}(\text{C}_6\text{F}_5)_4^-$), 137.1 (d, $^1J_{\text{CF}} = 246$, $\text{B}(\text{C}_6\text{F}_5)_4^-$), 129.8 (d, $^1J_{\text{CH}} = 158$, $\text{C}_{3,7}$), 125.2 (br, *ipso*- $\text{B}(\text{C}_6\text{F}_5)_4^-$), 120.9 (d, $^1J_{\text{CH}} = 154$, C_5), 47.3 (d, $^1J_{\text{CH}} = 138$, NCHMe_2), 27.8 (q, $^1J_{\text{CH}} = 125$, $\text{AlCH}_2\text{CHMe}_2$), 25.4 (d, $^1J_{\text{CH}} = 125$, $\text{AlCH}_2\text{CHMe}_2$), 23.9 (t, $^1J_{\text{CH}} = 115$, $\text{AlCH}_2\text{CHMe}_2$), 22.9 (q, $^1J_{\text{CH}} = 127$, NCHMe_2). Anal. Calcd for $\text{C}_{41}\text{H}_{28}\text{AlBF}_2\text{O}_2\text{N}_2$: C, 50.95; H, 2.92; N, 2.90. Found: C, 51.04; H, 3.15; N, 2.92.

EXAMPLE 55

Ethylene Polymerization by $[(i\text{Pr})_2\text{ATI})\text{Al}(i\text{Bu})][\text{B}(\text{C}_6\text{F}_5)_4]$

Toluene (ca. 15 mL) was added to a mixture of $[(i\text{Pr})_2\text{ATI})\text{Al}(i\text{Bu})_2$ (0.022 g, 0.064 mmol) and $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (0.066 g, 0.072 mmol). The mixture was stirred at 23 °C for 30 min and phase separation occurred. The mixture was degassed three times by the freeze/pump/thaw

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method. The mixture was heated to 80 °C, 1 atm of ethylene was introduced and the reaction mixture was stirred for 1 h at 80 °C. MeOH was added to the mixture and the resulting solid was collected by filtration, washed with MeOH and acetone, and dried under vacuum for 5 h affording 58 mg of polyethylene. Activity = 908 gPE/mol·h·atm.

EXAMPLE 56

10 Ethylene Polymerization by [$\{({}^i\text{Pr})_2\text{ATI}\}\text{Al}(\text{Et})\}[\text{B}(\text{C}_6\text{F}_5)_4]$.

Toluene (ca. 15 mL) was added to a mixture of [$\{({}^i\text{Pr})_2\text{ATI}\}\text{Al}(\text{Et})_2$] (0.015 g, 0.052 mmol) and [$\text{Ph}_3\text{C}\}\text{B}(\text{C}_6\text{F}_5)_4]$ (0.048 g, 0.052 mmol). The mixture was stirred at 23 °C for 30 min and phase separation occurred. The mixture was degassed three times by the freeze/pump/thaw method. The mixture was heated to 80 °C, 1 atm of ethylene was introduced and the reaction mixture was stirred for 1 h at 80 °C. MeOH was added to the mixture and the resulting solid was collected by filtration, washed with MeOH and acetone, and dried under vacuum for 5 h affording 136 mg of polyethylene. Activity = 2615 gPE/mol·h·atm.

EXAMPLE 57

25 Ethylene Polymerization by [$\{({}^i\text{Pr})_2\text{ATI}\}\text{Al}(\text{Et})\}[\text{B}(\text{C}_6\text{F}_5)_4]$.

A suspension of [$\text{Ph}_3\text{C}\}\text{B}(\text{C}_6\text{F}_5)_4]$ (189 mg, 204 μmol) in toluene (36 mL) in a Fisher-Porter bottle was placed in a 100 °C oil bath, and stirred for 20 min. The [$\text{Ph}_3\text{C}\}\text{B}(\text{C}_6\text{F}_5)_4]$ dissolved. The solution was then degassed under vacuum, and ethylene (1 atm) was introduced. A solution of [$\{({}^i\text{Pr})_2\text{ATI}\}\text{AlEt}_2$] (59.0 mg, 204 μmol) in toluene (3 mL) was added by syringe. The ethylene pressure was increased to 5 atm, and the solution was stirred for 30 min. The ethylene was vented, the Fisher-Porter bottle was opened to air, and acidified methanol (75 mL) was added. The mixture stirred overnight. The polyethylene was

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isolated by filtration, washed with acidified water (15 mL, 5 times), rinsed with acetone, and dried under vacuum for 16 h. Yield of polyethylene: 555 mg; activity: 1080 gPE/mol*h*atm.

5

EXAMPLE 58**Ethylene Polymerization by $[(i\text{Pr})_2\text{ATI}]\text{Al}(\text{Et})[\text{B}(\text{C}_6\text{F}_5)_4]$.**

10 The procedure described in example 57 was repeated. Yield of polyethylene: 520 mg; activity: 1010 gPE/mol*h*atm.

EXAMPLE 59

15 $[(i\text{Pr})_2\text{ATI}]\text{AlH}(\mu\text{-H})[\text{B}(\text{C}_6\text{F}_5)_4]$ ($(i\text{Pr})_2\text{ATI}]\text{AlH}_2$ (0.070 g, 0.30 mmol) and $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (0.139 g, 0.151 mmol) were placed in an NMR tube. C_6D_6 (ca. 0.5 mL) was added by vacuum transfer at -78°C . Phase separation was observed in the NMR tube and NMR analyses were performed on the lower layer. The analyses indicated the presence of $[(i\text{Pr})_2\text{ATI}]\text{AlH}(\mu\text{-H})[\text{B}(\text{C}_6\text{F}_5)_4]$ and Ph_3CH in the lower layer. ^1H NMR (C_6D_6): δ 6.95 (dd, $^3J_{\text{HH}} = 10.4, 10.1$, 4H, $\text{H}_{4,6}$), 6.53 (t, $^3J_{\text{HH}} = 9.5$, 2H, H_5), 6.52 (d, $^3J_{\text{HH}} = 10.8$, 4H, $\text{H}_{3,7}$), 4.54 (br, 3H, AlH), 3.28 (sept, $^3J_{\text{HH}} = 6.1$, 4H, NCHMe_2), 0.92 (d, $^3J_{\text{HH}} = 5.8$, 24H, NCHMe_2). ^{13}C NMR (C_6D_6): d 160.7 (s, $\text{C}_{2,8}$), 149.2 (d, $^1J_{\text{CF}} = 241$, $\text{B}(\text{C}_6\text{F}_5)_4^-$), 138.9 (d, $^1J_{\text{CF}} = 248$, $\text{B}(\text{C}_6\text{F}_5)_4^-$), 138.5 (d, $^1J_{\text{CH}} = 157$, $\text{C}_{4,6}$), 137.1 (d, $^1J_{\text{CF}} = 259$, $\text{B}(\text{C}_6\text{F}_5)_4^-$), 126.1 (d, $^1J_{\text{CH}} = 162$, $\text{C}_{3,7}$), 125.2 (br, ipso- $\text{B}(\text{C}_6\text{F}_5)_4^-$), 118.3 (d, $^1J_{\text{CH}} = 153$, C_5), 46.9 (d, $^1J_{\text{CH}} = 138$, NCHMe_2), 22.4 (q, $^1J_{\text{CH}} = 127$, NCHMe_2).

25
30

Resonances of Ph_3CH were also observed in the ^1H (δ 7.13-7.01 (m, 15H, Ph), 5.42 (s, 1H, Ph_3CH)) and ^{13}C (d 144.4 (s, ipso-Ph), 129.9 (d, $^1J_{\text{CH}} = 158$, o-Ph), 128.5 (d, $^1J_{\text{CH}} =$

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159, *m*-Ph), 126.4 (d, $^1J_{CH} = 160$, *p*-Ph), 57.5 (d, $^1J_{CH} = 127$, Ph_3CH) NMR spectra.

EXAMPLE 60

5 **{MeC(NAd)S}AlMe₃**. A suspension of adamantylisothio-cyanate AdN=C=S (1.35 g, 7.00 mmol) in hexanes (50 mL) was added to a rapidly stirred solution of AlMe₃ (0.70 mL, 7.3 mmol) in hexanes (20 mL). The mixture was stirred at room
10 temperature for 15 h to afford a slurry of a flocculent white precipitate in a yellow solution. The volatiles were removed under vacuum and {MeC(NAd)S}AlMe₂ was extracted with Et₂O (2 x 15 mL) and isolated from the extract by crystallization at -30 °C. Yield 1.52 g, 78%. **¹H NMR**
15 (CD₂Cl₂): δ 2.58 (s, 3H, CMe), 2.10 (br s, 3H, Ad-*H_g*), 1.95 (br d, $^2J_{HH} = 3.24$, 6H, Ad-*H_b*), 1.71 (br d, $^1J_{HH} = 14.4$, 3H, Ad-*H_d*), 1.67 (br d, $^1J_{HH} = 13.7$, 3H, Ad-*H_d*), -0.58 (s, 6H, AlMe₂). **¹³C NMR** (CD₂Cl₂): δ 196.0 (s, CMe), 58.9 (s, Ad-*C_a*), 42.3 (t, $^1J_{CH} = 127$, Ad-*C_b*), 36.3 (t, $^1J_{CH} = 126$, Ad-*C_d*), 29.9 (d, $^1J_{CH} = 133$, Ad-*C_g*), 29.4 (q, $^1J_{CH} = 130$, CMe), -8.8 (br q, AlMe₂). **Anal.** Calcd for C₁₄H₂₅AlNS: C, 63.12; H, 9.46; N, 5.26. Found: C, 63.32; H, 9.10; N, 5.11. The structure of this compound was confirmed by X-ray crystallography.

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EXAMPLE 61

{MeC(N^tBu)S}AlMe₂. A solution of AlMe₃ (1.04 g, 14.4 mmol) in hexanes (20 mL) was added to a rapidly stirred
30 solution *tert*-butylisothiocyanate (^tBuN=C=S, 1.56 g, 14.0 mmol) in hexanes (80 mL). The solution was stirred for 2 h after which time a white precipitate and yellow solution had formed. Removal of the volatiles under vacuum afforded pure {MeC(N^tBu)(S)}AlMe₂ as a yellow / orange liquid. Yield 2.32

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g, 86%. ^1H NMR (CD_2Cl_2): δ 2.54 (s, 3H, CMe), 1.35 (s, 9H, CMe₃), -0.59 (s, 6H, AlMe₂). ^{13}C NMR (CD_2Cl_2): δ 196.2 (s, CMe), 57.7 (s, CMe₃), 29.7 (q, $^1J_{\text{CH}}$ = 126, CMe₃), 28.6 (q, $^1J_{\text{CH}}$ = 130, CMe), -9.2 (br q, $^1J_{\text{CH}}$ = 112, AlMe₂).

5

EXAMPLE 62

{AdN(H)C(NAd)S}AlMe₂. A solution of AlMe₃ (0.210 g, 2.91 mmol) in hexanes (10 mL) was added to a suspension of bis(adamantyl)thiourea ((AdNH)₂C=S, 1.00 g, 2.90 mmol) in hexanes (80 mL). The solution became clear and a gas was evolved. After 15 h the volatiles were removed under vacuum to afford {AdN(H)C(NAd)(S)}AlMe₂ as a white solid (1.08 g, 93%). Analytically pure samples were obtained by recrystallization in Et₂O at 0°C. ^1H NMR (CD_2Cl_2): δ 5.38 (s, 1H, NH), 2.14 (s, 6H, Ad), 2.10 (br d, 6H, Ad), 1.90 (br d, 6H, Ad), 1.69 (s, 6H, Ad), 1.70 (br d, 3H, Ad), 1.64 (br d, 3H, Ad), -0.64 (s, 6H, AlMe₂). ^{13}C NMR (CD_2Cl_2): δ 171.1 (s, CNHAD), 54.8 (s, Ad-C α), * 42.7 (t, $^1J_{\text{CH}}$ = 129, Ad-C β), 42.4 (t, $^1J_{\text{CH}}$ = 127, Ad-C β), 36.6 (t, $^1J_{\text{CH}}$ = 127, Ad-C δ), 36.5 (t, $^1J_{\text{CH}}$ = 128, Ad-C δ), 30.2 (d, $^1J_{\text{CH}}$ = 133, Ad-C γ), 29.9 (d, $^1J_{\text{CH}}$ = 128, Ad-C γ), -7.7 (br q, $^1J_{\text{CH}}$ = 114, AlMe₂). * The two adamantyl C α peaks are coincident at δ 54.8. **Anal.** Calcd for C₂₃H₃₇AlN₂S: C, 68.96; H, 9.31; N, 6.99. Found: C, 68.78; H, 9.30; N, 6.91. The structure of this compound was confirmed by X-ray crystallography.

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EXAMPLE 63

{ArN(H)C(NAr)S}AlMe₂. This compound was prepared by the procedure described for {AdN(H)C(NAd)S}AlMe₂, using 1.00 g bis(2,6-diisopropylphenyl)thiourea (2.52 mmol) in 80 mL

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pentane, and 0.186 g AlMe₃ (2.58 mmol) in 10 mL pentane. After 15 h the volatiles were removed under vacuum yielding {ArN(H)C(NAr)(S)}AlMe₂ as a white solid. Yield 0.946 g, 83% based on AlMe₃. ¹H NMR (CD₂Cl₂): δ 7.36 (t, ³J_{HH} = 7.9, 1H, Ar-H_{para}), 7.27 (m, 3H, Ar), 7.19 (d, ³J_{HH} = 6.8, 2H, Ar-H_{meta}), 6.41 (br s, 1H, NH), 3.26 (sept, ³J_{HH} = 6.7, 2H, CHMe₂), 3.06 (sept, ³J_{HH} = 6.8, 2H, CHMe₂), 1.34 (d, ³J_{HH} = 6.8, 6H, CHMe₂), 1.33 (d, ³J_{HH} = 6.8, 6H, CHMe₂), 1.21 (d, ³J_{HH} = 6.1, 6H, CHMe₂), 1.08 (d, ³J_{HH} = 6.8, 6H, CHMe₂), -0.51 (s, 6H, AlMe₂). ¹³C NMR (CD₂Cl₂): δ 177.9 (s, CNHAr), 147.6 (s, Ar-C_{ortho}), 145.8 (s, Ar-C_{ortho}), 135.6 (s, Ar-C_{ipso}), 131.8 (s, Ar-C_{ipso}), 129.7 (d, ¹J_{CH} = 162, Ar-C_{para}), 128.0 (d, ¹J_{CH} = 160, Ar-C_{para}), 124.9 (d, ¹J_{CH} = 158, Ar-C_{meta}), 124.3 (d, ¹J_{CH} = 163, Ar-C_{meta}), 28.7 (d, ¹J_{CH} = 128, CHMe₂), 28.6 (d, ¹J_{CH} = 134, CHMe₂), 26.4 (q, ¹J_{CH} = 126, CHMe₂), 24.6 (q, ¹J_{CH} = 126, CHMe₂), 24.1 (q, ¹J_{CH} = 126, CHMe₂), 24.0 (q, ¹J_{CH} = 126, CHMe₂), -7.9 (q, ¹J_{CH} = 114, AlMe₂).

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EXAMPLE 64

{HC(CMeN^tBu)(CMeO)}AlMe₂. This compound was prepared by the procedure described for {HC(CMeNAr)₂}AlMe₂ (Ar = 2,6-ⁱPrC₆H₃), using 0.750 g HC(CMeN^tBu)(CMeO)H (4.83 mmol) in 60 mL hexanes, and 0.348 g AlMe₃ (4.83 mmol) in 10 mL hexanes. After 16 h the volatiles were removed to afford a yellow solid. Recrystallization from a concentrated Et₂O solution at -70 °C afforded pure {HC(CMeN^tBu)(CMeO)}AlMe₂ as a yellow crystalline solid. Yield 0.426 g, 42%. ¹H NMR (C₆D₆): δ 4.57 (s, 1H, CH), 1.70 (s, 3H, CMe), 1.58 (s, 3H, CMe), 1.20

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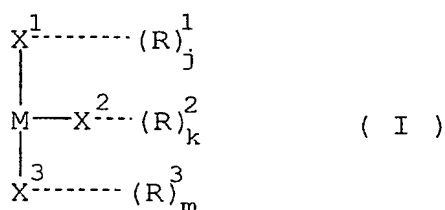
(s, 9H, CMe₃), -0.23 (s, 6H, AlMe₂). ¹³C NMR (C₆D₆): δ
177.2 (s, CMe), 175.5 (s, CMe), 101.3 (d, ¹J_{CH} = 158, CH),
57.1 (s, CMe₃), 31.3 (q, ¹J_{CH} = 126, CMe₃), 25.7 (q, ¹J_{CH} =
130, CMe), 24.9 (q, ¹J_{CH} = 127, CMe), -4.9 (br q, ¹J_{CH} =
5 107, AlMe₂). **Anal.** Calcd for C₁₁H₂₂AlNO: C, 62.53; H,
10.49; N, 6.63. The structure of this compound was
confirmed by X-ray crystallography.

CLAIMS

We claim:

1. A catalyst composition comprising three components, (1), (2) and (3), wherein:

Component (1) is a Lewis acid having the formula:



10

wherein

M is an atom selected from the Group 13 elements in the oxidation state of (III);

15 X^1 , X^2 and X^3 are the same or different and each is selected from hydrogen and the elements of Groups 14, 15, 16 and 17;

20 R^1 , R^2 and R^3 are the same or different and each is selected from hydrogen, hydrocarbyl, a substituted hydrocarbyl, a nitrogen- or oxygen-containing heterocyclic, silyl, siloxy groups or a metallic group and two groups (R^1 , R^2 or R^3) may be combined to form with X^1 , X^2 , or X^3 a cyclic group; and

25 j , k and m are the same or different and may be 0, 1, 2 or 3 as required to satisfy the valence of each of atoms X^1 , X^2 and X^3 to which R^1 , R^2 and R^3 , respectively, are bound;

30 Component (2) is a Lewis base having the formula $\text{Y}(\text{R}^4)_n$ wherein Y is an atom selected from the Group 15 and 16 elements; R^4 represents up to 3 substituents which may be the same or different and are selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, silyl, alkoxy,

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aryloxy and amino; n is 0, 1, 2 or 3 as required to satisfy the valence of Y to which R^4 is bound; two R^4 substituents may be joined groups which with Y form a cyclic group; and Component (2), $Y(R^4)_n$, is utilized in the range of 0 - 1,000 molar equivalents relative to Component (1); and

Component (3) is an activator selected from (a) a salt of a labile, weakly coordinating or non-coordinating anion that is capable of abstracting one of the $-X^1--(R^1)_j$, $-X^2--(R^2)_k$ or $-X^3--(R^3)_m$ groups from Component (1); (b) a neutral Lewis-acid that is capable of abstracting one of the $-X^1--(R^1)_j$, $-X^2--(R^2)_k$ or $-X^3--(R^3)_m$ groups from Component (1); (c) an oxidizing agent capable of reacting with Component (1) and converting it to a cationic derivative; and (d) alumoxanes in a molar ratio of Components (1):(3) from 1:0.001-100,000.

2. A catalyst composition according to Claim 1 wherein M is aluminum or gallium.
3. A catalyst composition according to Claim 1 wherein M is aluminum.
4. A catalyst composition according to Claim 1 wherein Components (1) and (2) constitute a Lewis-base complex of the Component (1) Lewis acid and the Component (2) Lewis base.
5. A catalyst composition according to Claim 1 consisting essentially of Components (1) and (3).
6. A catalyst composition according to Claim 2 wherein $-X^1--(R^1)_j$, $-X^2--(R^2)_k$ and $-X^3--(R^3)_m$ are the same or different and each represents hydrogen, alkyl of up to about 12 carbon atoms, bromide or chloride.

7. A catalyst composition according to Claim 4 wherein Component (2) is selected from ethers, trialkyl-amines, pyridines, imines, anilines, phosphines and phosphites.
- 5 8. A catalyst composition according to Claim 2 wherein Component (3) is (a) a salt selected from borate and aluminate salts; (b) a neutral Lewis-acid selected from boranes and alanes; (c) an oxidizing agent selected from ferrocenium or silver (I) salts of non-coordinating or
10 weakly coordinating anions; or (d) methylalumoxane in a molar ratio to Component (1) within the range of 1:0.1-1,000.
- 15 9. A supported catalyst comprising Components (1), (2), and (3), as defined in Claim 2, codeposited on a catalyst support material.
- 20 10. A supported catalyst according to Claim 9 wherein the catalyst support material is a polyolefin prepolymer, magnesium oxide, magnesium chloride, silica, alumina or carbon.
- 25 11. A process for the preparation of a polymer of a polymerizable, unsaturated compound which comprises contacting a polymerizable, unsaturated compound with a catalyst composition defined in Claim 1 under polymerization conditions of temperature and pressure.
- 30 12. A process according to Claim 11 wherein the polymerizable, unsaturated compound comprises at least one α -olefin containing from 2 to 8 carbon atoms.
- 35 13. A process according to Claim 11 wherein the polymerizable, unsaturated compound comprises ethylene.
14. A process according to Claim 11 wherein the

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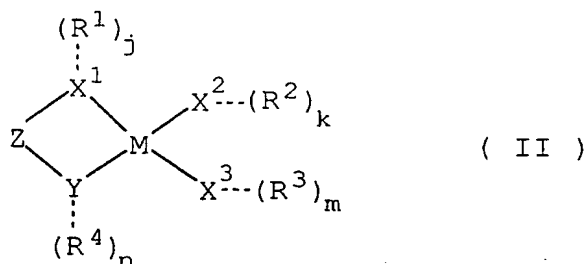
polymerization conditions comprise a temperature of 0 to 300°C and a pressure of 1 to 1500 atmospheres.

15. A process according to Claim 11 wherein the
5 polymerization is carried out in a slurry mode of operation.
16. A process according to Claim 11 wherein the
10 polymerization is carried out in a solution mode of operation.
17. A process according to Claim 11 wherein the
15 polymerization is carried out in a bulk phase using either solution or slurry modes of operation.
18. A process according to Claim 11 wherein the
polymerization is carried out at a pressure in the range of 10 to 200 atmospheres.
- 20 19. A catalyst composition comprising two components, (3) and (4), wherein

Component (3) is an activator selected from (a) a salt of a labile, weakly coordinating or non-coordinating
25 anion that is capable of abstracting one of the $-X^2--(R^2)_k$ or $-X^3--(R^3)_m$ groups from Component (4); (b) a neutral Lewis-acid that is capable of abstracting one of the $-X^2--(R^2)_k$ or $-X^3--(R^3)_m$ groups from Component (4); (c) an oxidizing agent capable of reacting with
30 Component (4) and converting it to a cationic derivative; and (d) alumoxanes in a molar ratio of Components (4):(3) from 1:0.001-100,000; and

Component (4) is a Group 13 metal complex having the
35 formula:

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wherein

M is an atom selected from the Group 13 elements in the oxidation state of (III);

X^1 is selected from the elements of Groups 14, 15 and 16;

X^2 and X^3 are the same or different and each is selected from hydrogen and the elements of Groups 14, 15, 16 and 17;

Y is an atom selected from the Group 14, 15 and 16 elements;

R^1 are the same or different and each is selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, a nitrogen- or oxygen-containing heterocyclic, alkoxy, amino, or silyl groups and two groups (R^1) may be combined to form with X^1 a cyclic group;

R^2 and R^3 are the same or different and each is selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, a nitrogen- or oxygen-containing heterocyclic group, silyl, alkoxy, amino, siloxy or a metallic group and two groups (R^2 or R^3) may be combined to form with X^2 or X^3 a cyclic group;

R^4 represent up to 3 substituents which may be the same or different and are selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, a nitrogen- or oxygen-containing heterocyclic, silyl, alkoxy, aryloxy or amino groups and two R^4 groups may be combined to form with Y a cyclic group;

j, k, m and n are the same or different and may be 0,

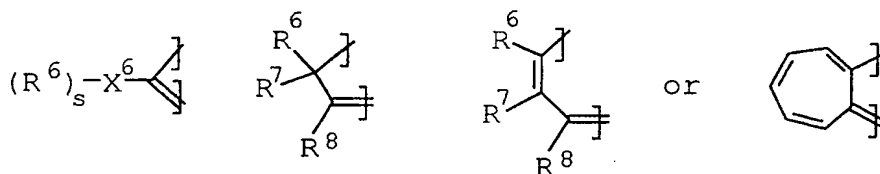
1, 2 or 3 as required to satisfy the valence of each of atoms X^1 , X^2 , X^3 and Y to which R^1 , R^2 , R^3 , and R^4 , respectively, are bound; and

Z if present is a saturated or unsaturated linking group.

20. A catalyst composition according to Claim 19 wherein M of Component (4) is selected from aluminum and gallium.

21. A catalyst composition according to Claim 19 wherein M of Component (4) is aluminum.

22. A catalyst composition according to Claim 20 wherein Z of Component (4), if present, is selected from



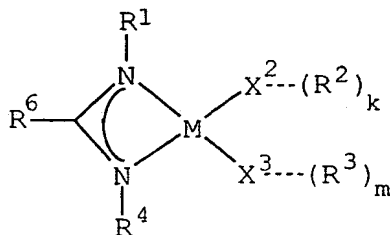
unsaturated linking groups having the structures:

wherein R^6 , R^7 and R^8 are the same or different and each is selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, or silyl groups with 1 to about 30 carbon atoms; X^6 is an oxygen, nitrogen, carbon or silicon atom; s is 1, 2, or 3 as required to satisfy the valence of X^6 ; and any two groups (R^6 , R^7 and R^8) may be combined to form with X^1 , X^6 or Y a cyclic group.

23. A catalyst composition according to Claim 20 wherein X^1 and Y of Component (4) are nitrogen atoms.

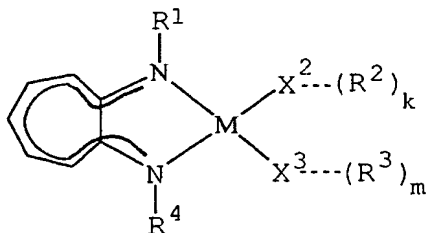
24. A catalyst composition according to Claim 23 wherein R^1 and R^4 are independently selected from hydrocarbyl, substituted hydrocarbyl, or silyl groups of 1 to about 30 carbon atoms; and j and n each is 1.

25. A catalyst composition according to Claim 24 in which Component (4) has the formula:

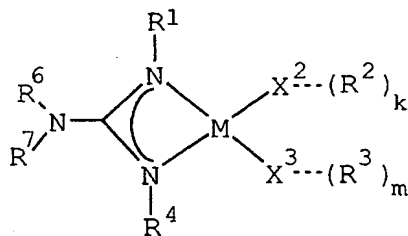


- 5 wherein R⁶ is selected from a hydrocarbyl, sub-stituted hydrocarbyl or a silyl group containing less than 30 carbon atoms.

26. A catalyst composition according to Claim 24 in which Component (4) has the formula:



27. A catalyst composition according to Claim 24 in which Component (4) has the formula:



- 15 wherein R⁶ and R⁷ are the same or different and each is selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, or silyl groups with 1 to about 30 carbon atoms and the groups R¹, R⁴, R⁶ and R⁷ may be combined so
20 as to form cyclic groups.

28. A catalyst composition according to Claim 20 wherein $-X^2--(R^2)_k$ and $-X^3--(R^3)_m$ represent hydrogen, hydrocarbyl, or halogen.

29. A catalyst composition according to Claim 28 wherein $-X^2--(R^2)_k$ and $-X^3--(R^3)_m$ represent alkyls of up to about 12 carbon atoms, bromide or chloride.

30. A catalyst composition according to Claim 20 wherein Component (3) is (a) a salt selected from borate and aluminate salts; (b) a neutral Lewis-acid selected from boranes and alanes; (c) an oxidizing agent selected from ferrocenium or silver (I) salts of non-coordinating or weakly coordinating anions; or (d) methylalumoxane in a molar ratio of Components (4):(3) from 1:0.1-1,000.

31. A supported catalyst comprising Components (3) and (4), as defined in Claim 19, codeposited on a catalyst support material.

32. A supported catalyst according to Claim 31 wherein the catalyst support material is a polyolefin prepolymer, magnesium oxide, magnesium chloride, silica, alumina or carbon.

33. A process for the preparation of a polymer of a polymerizable, unsaturated compound which comprises contacting a polymerizable, unsaturated compound with a catalyst composition defined in Claim 20 under polymerization conditions of temperature and pressure.

34. A process according to Claim 33 wherein the polymerizable, unsaturated compound comprises at least one α -olefin containing from 2 to 8 carbon atoms.

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35. A process according to Claim 33 wherein the polymerizable, unsaturated compound comprises ethylene.

36. A process according to Claim 33 wherein the polymerization conditions comprise a temperature of 0 to 300°C and a pressure of 1 to 1500 atmospheres.

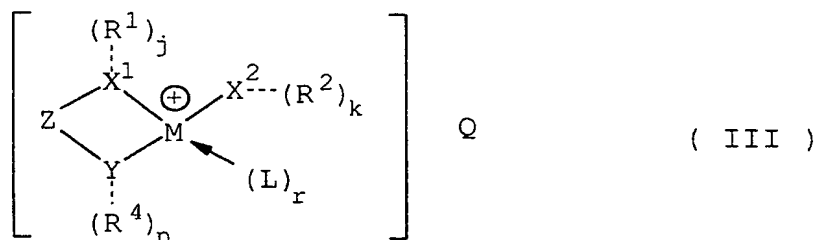
37. A process according to Claim 33 wherein the polymerization is carried out in a slurry mode of operation.

38. A process according to Claim 33 wherein the polymerization is carried out in a solution mode of operation.

39. A process according to Claim 33 wherein the polymerization is carried out in a bulk phase using either solution or slurry modes of operation.

40. A process according to Claim 33 wherein the polymerization is carried out at a pressure in the range of 10 to 200 atmospheres.

41. A catalyst composition comprising a single component cationic Group 13 complex compound (5) having the formula:



wherein

M is an atom selected from the Group 13 elements in the oxidation state of (III);

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X^1 is selected from the elements of Groups 14, 15 and 16;

X^2 is selected from the elements of Groups 14, 15, 16 and 17;

5 Y is an atom selected from the Group 14, 15 and 16 elements;

10 R^1 are the same or different and each is selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, a nitrogen- or oxygen-containing heterocyclic, alkoxy, amino, or silyl groups and two groups (R^1) may be combined to form with X^1 a cyclic group;

15 R^2 are the same or different and each is selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, a nitrogen- or oxygen-containing heterocyclic, silyl, alkoxy, amino, siloxy groups or a metallic group and two groups (R^2) may be combined to form with X^2 a cyclic group;

20 R^4 represent up to 3 substituents which may be the same or different and are selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, nitrogen- or oxygen-containing heterocyclic, silyl, alkoxy and amino groups and two groups (R^4) may be combined to form with Y a cyclic group;

25 j , k and n are the same or different and may be 0, 1, 2 or 3 as required to satisfy the valence of each of atoms X^1 , X^2 and Y to which R^1 , R^2 , and R^4 , respectively, are bound;

r is 0-3;

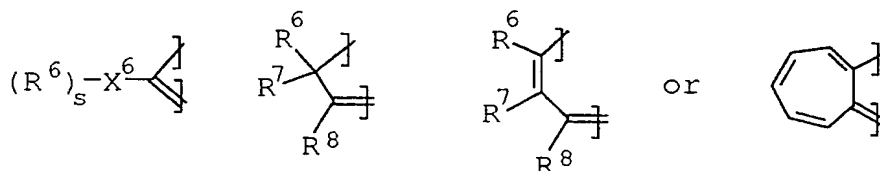
30 Z if present is a saturated or unsaturated linking group;

L if present is a neutral Lewis base, donor ligand or a neutral or cationic Group 13 metal species which coordinates through a bridging group; and

35 Q is a non-coordinating or weakly coordinating anionic group.

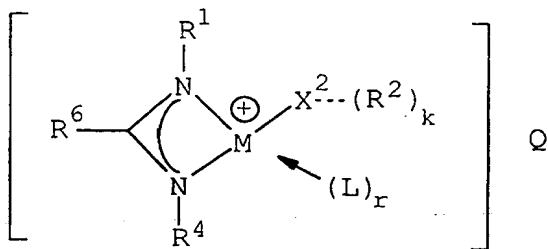
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42. A cationic Group 13 complex compound according to Claim 41 wherein M is selected from aluminum and gallium.
43. A cationic Group 13 complex compound according to Claim 41 wherein M is aluminum.
44. A cationic Group 13 complex compound according to Claim 42 wherein Z, if present, is selected from unsaturated linking groups having the structures:



- wherein R^6 , R^7 and R^8 are the same or different and each is selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, or silyl groups with 1 to about 30 carbon atoms; X^6 is an oxygen, nitrogen, carbon or silicon atom; s is 1, 2, or 3 as required to satisfy the valence of X^6 ; and any two groups (R^6 , R^7 and R^8) may be combined to form with X^1 , X^6 or Y a cyclic group.

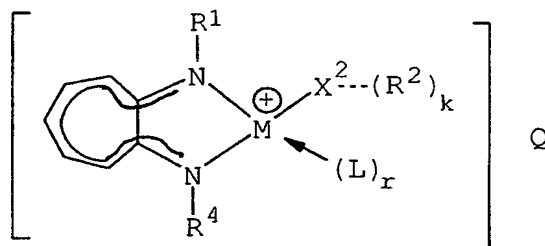
45. A cationic Group 13 complex compound according to Claim 42 wherein X^1 and Y are nitrogen atoms.
46. A cationic Group 13 complex compound according to Claim 45 wherein R^1 and R^4 are independently selected from hydrogen, alkyl of 1 to about 30 carbon atoms, or silyl; and j and n each is 1.
47. A cationic Group 13 complex compound according to Claim 46 having the formula:



wherein R⁶ is selected from a hydrocarbyl, substituted hydrocarbyl, or a silyl group containing less than 30 carbon atoms.

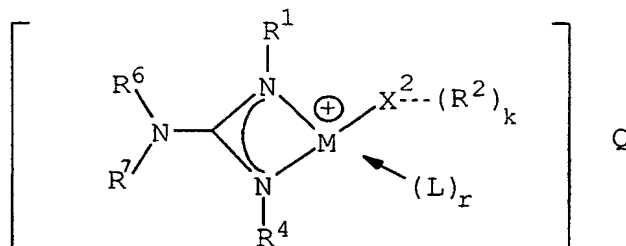
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48. A cationic Group 13 complex compound according to Claim 46 having the formula:



49. A cationic Group 13 complex compound according to Claim 46 having the formula:

10



wherein R⁶ and R⁷ are the same or different and each is selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, or silyl groups with 1 to about 30 carbon atoms and the groups R¹, R⁴, R⁶ and R⁷ may be combined so as to form cyclic groups.

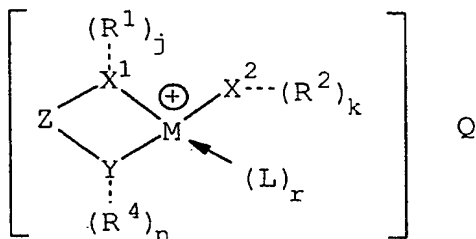
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50. A cationic Group 13 complex compound according to Claim 42 wherein L is an ether, pyridine, or aniline compound or a neutral or cationic Group 13 derivative.
- 5 51. A cationic Group 13 complex compound according to Claim 42 wherein $-X^2--(R^2)_k$ represents hydrogen, hydrocarbyl, or halogen.
- 10 52. A cationic Group 13 complex compound according to Claim 51 wherein $-X^2--(R^2)_k$ represents alkyl of up to about 12 carbon atoms, iodide, bromide or chloride.
- 15 53. A cationic Group 13 complex compound according to Claim 42 wherein Q is a borate or aluminumate anion.
54. A cationic Group 13 complex compound according to Claim 53 wherein Q is a triarylborate anion with three pentafluorophenyl or 3,5-bis-trifluoromethyl-phenyl groups and one $-X^2--(R^2)_k$ as defined in Claim 52.
- 20 55. A supported catalyst comprising a cationic Group 13 complex compound (5) defined in Claim 42 deposited on a catalyst support material.
- 25 56. A supported catalyst according to Claim 55 wherein the catalyst support material is a polyolefin prepolymer, magnesium oxide, magnesium chloride, silica, alumina or carbon.
- 30 57. A process for the preparation of a polymer of a polymerizable, unsaturated compound which comprises contacting a polymerizable, unsaturated compound with a catalyst composition defined in Claim 42 under polymerization conditions of temperature and pressure.
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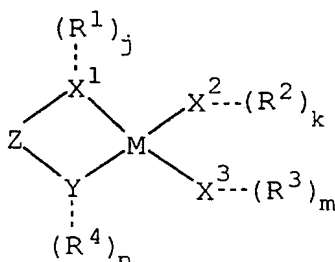
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58. A process according to Claim 57 wherein the polymerizable, unsaturated compound comprises at least one α -olefin containing from 2 to 8 carbon atoms.
- 5 59. A process according to Claim 57 wherein the polymerizable, unsaturated compound comprises ethylene.
60. A process according to Claim 57 wherein the polymerization conditions comprise a temperature of 0 to 160°C and a pressure of 1 to 500 atmospheres.
- 10 61. A process according to Claim 57 wherein the polymerization is carried out in a slurry mode of operation.
- 15 62. A process according to Claim 57 wherein the polymerization is carried out in a solution mode of operation.
- 20 63. A process according to Claim 57 wherein the polymerization is carried out in a bulk phase using either solution or slurry modes of operation.
- 25 64. A process according to Claim 57 wherein the polymerization is carried out at a pressure in the range of 10 to 200 atmospheres.
65. A process for the preparation of a cationic Group 13 complex compound having the formula:



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which comprises reacting a neutral precursor complex having the formula:



5 wherein

M is an atom selected from the Group 13 elements in the oxidation state of (III);

X¹ is selected from the elements of Groups 14, 15 and 16;

10 X² and X³ are the same or different and each is selected from hydrogen and the elements of Groups 14, 15, 16 and 17;

Y is an atom selected from the Group 14, 15 and 16 elements;

15 R¹ are the same or different and each is selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, a nitrogen- or oxygen-containing heterocyclic, alkoxy, amino, or silyl groups and two groups (R¹) may be combined to form with X¹ a cyclic group

20 R² and R³ are the same or different and each is selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, a nitrogen- or oxygen-containing heterocyclic, alkoxy, amino, silyl, siloxy groups or a metallic group and two groups (R² or R³) may be combined to form with X² or X³ a cyclic group;

25 R⁴ represent up to 3 substituents which may be the same or different and are selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, a nitrogen- or oxygen-containing heterocyclic group, silyl, alkoxy, and amino and two R⁴ groups may be combined to form with Y a

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cyclic group;

j, k, m and n are the same or different and may be 0, 1, 2 or 3 as required to satisfy the valence of each of atoms X^1 , X^2 , X^3 and Y to which R^1 , R^2 , R^3 , and R^4 , respectively, are bound; and

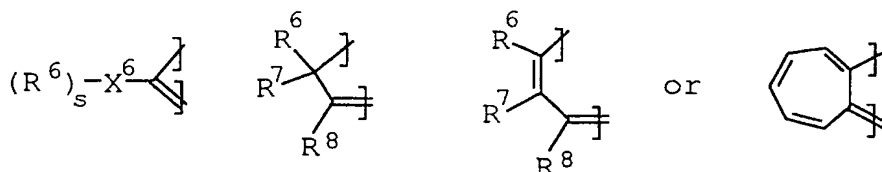
Z if present is a saturated or unsaturated linking group;

with an activator compound selected from (a) a salt of a labile, weakly coordinating or non-coordinating anion that is capable of abstracting one of the $-X^2--(R^2)_k$ or $-X^3--(R^3)_m$ groups from the neutral precursor complex; (b) a neutral Lewis-acid that is capable of abstracting one of the $-X^2--(R^2)_k$ or $-X^3--(R^3)_m$ groups from the neutral precursor complex; (c) an oxidizing agent capable of reacting with the neutral precursor complex and converting it to a cationic derivative.

66. The process according to Claim 65 wherein M is selected from aluminum and gallium.

67. The process according to Claim 65 wherein M is aluminum.

68. The process according to Claim 66 wherein Z of the neutral precursor complex is selected from unsaturated linking groups having the structures:



wherein R^6 , R^7 and R^8 are the same or different and each is selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, or silyl groups with 1 to about 30 carbon atoms; X^6 is an oxygen, nitrogen, carbon or silicon atom;

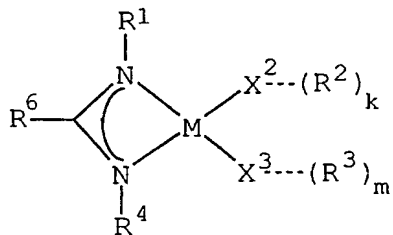
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s is 1, 2, or 3 as required to satisfy the valence of X^6 ; and any two groups (R^6 , R^7 and R^8) may be combined to form with X^1 , X^6 or Y a cyclic group.

5 69. The process according to Claim 66 wherein X^1 and Y of the neutral precursor complex are nitrogen atoms.

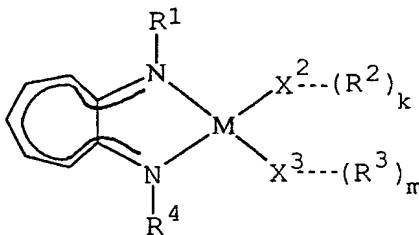
70. The process according to Claim 69 wherein R^1 and R^4 are independently selected from hydrocarbyl, substituted
10 hydrocarbyl, or silyl groups of 1 to about 30 carbon atoms; and j and n each is 1.

71. The process according to Claim 70 in which the neutral precursor complex has the formula:

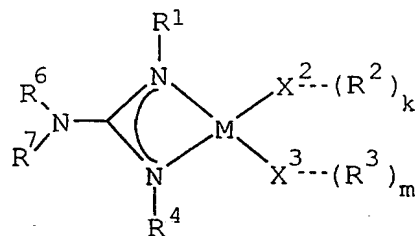


15 wherein R^6 is selected from a hydrocarbyl, substituted hydrocarbyl, or a silyl group containing less than 30 carbon atoms.

20 72. The process according to Claim 70 in which the neutral precursor complex has the formula:



73. The process according to Claim 70 in which the neutral precursor complex has the formula:



wherein R⁶ and R⁷ are the same or different and each is selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, or silyl groups with 1 to about 30 carbon atoms and the groups R¹, R⁴, R⁶ and R⁷ may be combined so as to form cyclic groups.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/04895

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08F10/00 C08F4/54 B01J31/18 B01J31/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

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IPC 6 C08F B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 747 403 A (FINA TECHNOLOGY) 11 December 1996 see claim 1; page 4, example 1	1-3, 11, 12, 14, 15, 17
A	GB 2 295 393 A (ASS OCTEL) 29 May 1996 see claims; examples	19-25, 28, 29
A	GB 957 391 A (HERCULES POWDER) 6 May 1964 see claims; page 2, lines 25-36	1, 19, 41

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☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

18 June 1998

Date of mailing of the international search report

26/06/1998

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Information on patent family members

Inter national Application No

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0747403 A	11-12-1996	US 5643846 A JP 9100310 A	01-07-1997 15-04-1997
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GB 957391 A		BE 619439 A DE 1520055 A FR 1333249 A NL 280229 A US 3186958 A	12-02-1970 16-12-1963 01-06-1965



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C08F 10/00, 4/54, B01J 31/18, 31/16	A1	(11) International Publication Number: WO 98/40421 (43) International Publication Date: 17 September 1998 (17.09.98)
(21) International Application Number: PCT/US98/04895 (22) International Filing Date: 12 March 1998 (12.03.98) (30) Priority Data: 08/818,297 14 March 1997 (14.03.97) US 60/068,641 23 December 1997 (23.12.97) US 09/033,489 3 March 1998 (03.03.98) US (71) Applicant: UNIVERSITY OF IOWA RESEARCH FOUNDATION [US/US]; Oakdale Research Campus, 100 Oakdale Campus #214, Iowa City, IA 52242-5000 (US). (72) Inventors: JORDAN, Richard, F.; Oakdale Research Campus, 100 Oakdale Campus #214, Iowa City, IA 52242-5000 (US). COLES, Martyn, P.; Oakdale Research Campus, 100 Oakdale Campus #214, Iowa City, IA 52242-5000 (US). DAGORNE, Samuel; Oakdale Research Campus, 100 Oakdale Campus #214, Iowa City, IA 52242-5000 (US). IHARA, Eiji; Oakdale Research Campus, 100 Oakdale Campus #214, Iowa City, IA 52242-5000 (US). (74) Agent: SEASE, Edmund, J.; Zarley, McKee, Thomte, Voorhees & Sease, Suite 3200, 801 Grand Avenue, Des Moines, IA 50309-2721 (US).		(81) Designated States: CA, DE, GB, JP, KR, MX, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: CATIONIC GROUP 13 COMPLEXES INCORPORATING BIDENTATE LIGANDS AS POLYMERIZATION CATALYSTS		
(57) Abstract <p>Disclosed are novel catalysts, processes of synthesizing the catalysts and olefin polymerization processes using the catalysts. The catalysts are cationic complexes comprising a Group 13 element and certain ligands. These compounds behave similarly to Ziegler-Natta catalysts but effectively catalyze the polymerization of olefins in the absence of any transition metal.</p>		

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